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Removal of copper and iron contamination from
chromic acid electroplating baths using
electrodialysis with caustic catholyte.

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REMOVAL OF COPPER AND IRON CONTAMINATION
FROM CHROMIC ACID ELECTROPLATING BATHS
USING ELECTRODIALYSIS WITH CAUSTIC CATHOLYTE

A Special Research Problem
Presented to
The Faculty of the School of Civil Engineering

by

John T. Sommer

In Partial Fulfillment
of the Requirements for the Degree of
Master of Science in Environmental Engineering

June 1991

GEORGIA INSTITUTE OF TECHNOLOGY
A UNIT OF THE UNIVERSITY SYSTEM OF GEORGIA
SCHOOL OF CIVIL ENGINEERING
ATLANTA, GEORGIA 30332



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ABSTRACT

The efficiency and kinetics of the removal of copper and iron contamination from a chromic acid plating bath were evaluated using a proprietary electrodialytic purification unit with caustic catholyte. The unit consisted of an anode compartment and a cathode compartment separated by a cation-specific membrane. The proprietary electrodes in each compartment were connected to a constant amperage, variable voltage power supply.

By design, multivalent metal cations were electrotransported through the membrane and converted into insoluble hydroxides upon reaction with cathode-formed hydroxyl ions and other insolubilizing agents present in the proprietary catholyte solution. Threshold Contaminant Levels (TCLs) were approximated using the Hull Cell test apparatus and sample metal concentrations were measured using atomic absorption spectrophotometry.

The feasibility and applicability of this technology for the purification of typical chromic acid plating baths will be discussed.

1.0 INTRODUCTION

1.1 Research Objective

The objective of this research was to evaluate the effectiveness of the purification technology of electrodialysis using caustic catholyte as applied to the removal of typical metal contaminants from a chromic acid electroplating bath. The kinetics and efficiency of contaminant removal were studied in an effort to determine power and sizing requirements as well as the overall suitability of electrodialysis for chromic acid plating bath purification in a closed-loop process.

Copper (Cu) and iron (Fe) contamination were chosen based on their prevalency in the electroplating industry as indicated by the literature. A proprietary, bench-scale electrodialytic purification unit (IONSEP™ 2C Mini Cell) was furnished to the Georgia Institute of Technology by the manufacturer (IONSEP Corporation, Rockland, Delaware) for this evaluation.

Prior to treatment of the test plating bath using electrodialysis, threshold contamination levels were approximated using the Hull Cell test procedure and information gained from industry experts. Atomic absorption spectrophotometry was used for quantitative metals analysis.

1.2 Background

1.2.1 Electroplating -

Electroplating is one of several processes in the broader category of metal finishing (Standard Industrial Classification

3471). The Environmental Protection Agency (EPA) has divided the metal finishing industry into two segments, electroplating and metal finishing, for regulatory purposes. Electroplating is defined as the application of a surface coating to improve the surface and structural surface properties of metals and other materials.(1) Metal finishing through surface electroplating allows one to use inexpensive and abundant metals (such as steel and zinc) for the bulk of a finished product while giving the exterior of the product the properties needed for its productive use.

The plating industry utilizes many chemical and electrochemical reactions to apply these surface treatments. Many of the effluents and by-products generated during these processes in an electroplating plant are highly toxic and corrosive. These wastes are considered hazardous as they contain high levels of heavy metals and organic solvents.

1.2.2 Industry Regulation -

Until the mid-1970's there were virtually no limits placed on the amount and nature of disposed electroplating wastes and, as a result, they were generally landfilled, representing a potentially serious threat to surface and groundwater purity. In October of 1986, on the heels of the Resource Conservation and Recovery Act (RCRA) of 1976 and the Hazardous and Solid Waste Amendment (HSWA) of 1984, the EPA submitted a "Report to Congress on Minimization of Hazardous Wastes". This report, along with the Agency's "Waste Minimization Strategy" released in 1987,

emphasized a shift in the management of toxic and industrial wastes from end-of-the-pipe procedures and disposal (landfilling) to the adoption of actual waste minimization or pollution prevention (the broader term currently favored by the EPA (2)) measures in all aspects of industrial processes.

1.2.3 Chromium -

Chromium is an elemental metal found naturally as a chromite (FeCr_2O_4). It was first electroplated from a solution of chromic acid with sulfite catalyst in about 1890 (3). Chromium is highly toxic to human beings and is included in the EPA list of priority pollutants (4). It exists in two distinct oxidation states in the environment: hexavalent (Cr^{+6}) and trivalent (Cr^{+3}). At sufficiently high concentrations, hexavalent chromium is known to inhibit the operations of a publicly owned treatment works (POTW). For activated sludge operations levels as low as 1 mg/L have adverse results and concentrations of approximately 5 mg/L deter anaerobic digestion. Nitrification processes may be inhibited at values as low as 0.25 mg/L chromium. (5) It has been shown that between 60 and 80% of the chromium introduced into a POTW is allowed to pass through (6). The chromium that passes through the POTW is discharged to ambient surface water. Chromium is known to accumulate within the body and can cause serious poisoning within a short amount of time. Hexavalent chromium is a known carcinogen and it promotes bronchial asthma, ulcers, and a wide range of skin ailments. It has also been shown to be mutagenic (7). Hexavalent chromium is generally

believed to be the more toxic of the oxidation states, however, there is substantial evidence of trivalent chromium also being highly toxic.

1.2.4 Waste Generation -

Every year thousands of tons of inorganic wastes are generated in various chemical and electrochemical processes involved in electroplating. In general, waste is a concrete example of process inefficiency. From an economic standpoint, waste represents the inefficient use of process chemicals and raw materials and results in increased manufacturing costs. Furthermore, higher volumes of generated hazardous wastes represent a direct drain on profit dollars due to the ever-increasing costs associated with proper treatment and disposal. Perhaps even more importantly, they pose a threat to a safe and healthy environment. In an effort to increase profit, reduce operator liability, and progress towards minimization of environmental risk and impact, pollution prevention (as opposed to after-the-fact pollution treatment) has become the focus of plating waste management programs.

For chrome electroplating, current estimates indicate that about 60 million pounds of chromium compounds are landfilled each year. This volume of waste is put into perspective by knowing that for some chromic acid solutions the cost of treatment, hauling, and landfill approaches \$12 per gallon. (3)

1.2.5 U. S. Navy Plating Operations -

The United States Navy operates a large number of electroplating facilities at various bases throughout the United States. The Naval Civil Engineering Laboratory, Port Hueneme, California, in support of the Naval Facilities Engineering Command has been tasked with identifying and evaluating innovative and cost effective technologies for the recovery, reuse, and purification of the more than 500,000 gallons of spent metal finishing baths generated annually at naval installations. Dollar values associated with the cost of disposal/treatment of these wastes exceed \$4 million. The majority of Navy electroplating operations (approximately 60%) utilizes chromium (Cr) plating baths. (8,9) Most of the chrome plating performed is Hard Chromium plating for the repair of ship and aircraft parts.

1.2.6 Plating Waste Minimization -

Strategies for the reduction of waste in the electroplating industry are classified as follows (10): 1) Source Reduction, 2) Recycling and Resource Recovery, or 3) Alternative Treatment. Waste minimization techniques in electroplating consist primarily in efforts to minimize rinse water consumption, recover baths and rinses, substitute less toxic raw materials, and extend plating bath life. Spent (contaminated) plating baths are the greatest potential source of hazardous waste in electroplating operations (10). It is in the extension of plating bath lives and the recovery of baths that conservation of raw materials and

reduction in the generation of hazardous wastes requiring treatment and/or disposal can be best achieved. It is also in these areas that the application of existing or innovative technologies is beneficial. This approach falls in the Recycling and Resource Recovery category.

In the past, treatment of spent chromium plating baths involved the reduction of hexavalent chromium to the trivalent state, followed by its precipitation as hydroxide with either sodium hydroxide, sodium carbonate, or calcium hydroxide. Two reducing agents were used for this purpose: sulfur dioxide gas or sodium bisulfite in an acid solution (11). Removal of soluble metallic contaminants through precipitation as insoluble metal hydroxides was accomplished through pH adjustment using sodium hydroxide, sodium carbonate, or calcium hydroxide. The resultant sludge from both these processes traditionally was dumped in landfills, no longer a viable solution with respect to economics, regulatory constraints, and environmental responsibility.

The answer to waste minimization in the chrome plating industry lies in effective in-line plating bath treatment processes. Technologies for the purification of chromium plating baths can be placed in three major categories: 1) ion exchange, 2) electrolysis, and 3) electrodialysis. The application of these methods falls under either the removal of metallic impurities or the conversion of trivalent chromium (Cr^{+3}) back to the desired hexavalent form (Cr^{+6}). Table 1.2 lists the applications of variations of the three major technologies.(12)

Table 1.2: Chromium Solution Purification Technologies

<u>Technology</u>	<u>Cr⁺³ Oxidation/Removal</u>	<u>Metal Removal</u>
Ion Exchange	Yes	Yes
Electrolysis		
w/out diffused barrier	Yes	No
w/diffused barrier	Yes	Yes
Electrodialysis		
Acidic catholyte	Yes	Yes
Caustic catholyte	Yes	Yes

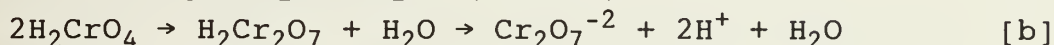
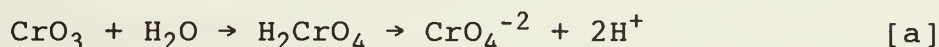
1.3 Electroplating Process

Electroplating occurs when metal ions in solution are reduced on cathodic surfaces due to the application of a direct electrical current. The result is a plated exterior layer on the cathodes, or the parts to be plated. The replenishment of the metal ions in solution is achieved through the dissolution of metal from soluble anodes, from small pure metal pieces placed in the solution, or, as in the case of chromium plating, from metal salts placed in the solution.

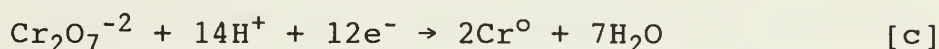
All practical chromium plating is done from a solution consisting mainly of hexavalent chromium oxide, CrO₃, (commonly referred to as chromic acid) plus small, but critical, quantities of an anion, usually sulfate or a complex fluoride (13). In general, the only variations in the field of chromium plating are in the concentration of chromic acid in the bath, the amount and nature of the catalyst, and in operating conditions.

There are a number of proposed theories to explain the mechanism of hexavalent chromium electroplating. Most of them resemble the following multiple reactions (14,15).

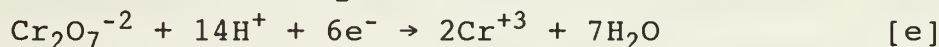
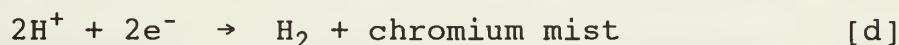
Dissolution Reaction:



Deposition Reaction:



Side Reactions:



Reaction [c] typically has an efficiency of 20% or less and is achieved in the presence of the required catalyst, e.g. sulfate.

Reaction [d] consumes 80% or more of the available power.

Reaction [f] occurs at the inert anode.

Most plating baths have the metal, M, present in solution as a cation, M^+ , however with chromium plating, chromium metal is present as an anion complex, $\text{Cr}_2\text{O}_7^{2-}$, which very likely undergoes further complexing with other present ions such as the sulfate catalyst to permit chromium deposition as shown in reaction [c] (11). Chromium plating baths also differ from other types of plating baths in that they are operated with insoluble anodes and are replenished through the controlled addition of metal salts

(chromic acid). The pH of these plating baths is maintained below three with little problem, however the addition of ammonia or hydrochloric acid can be used, if required, with little or no effect (16).

1.4 Chrome Plating Operations

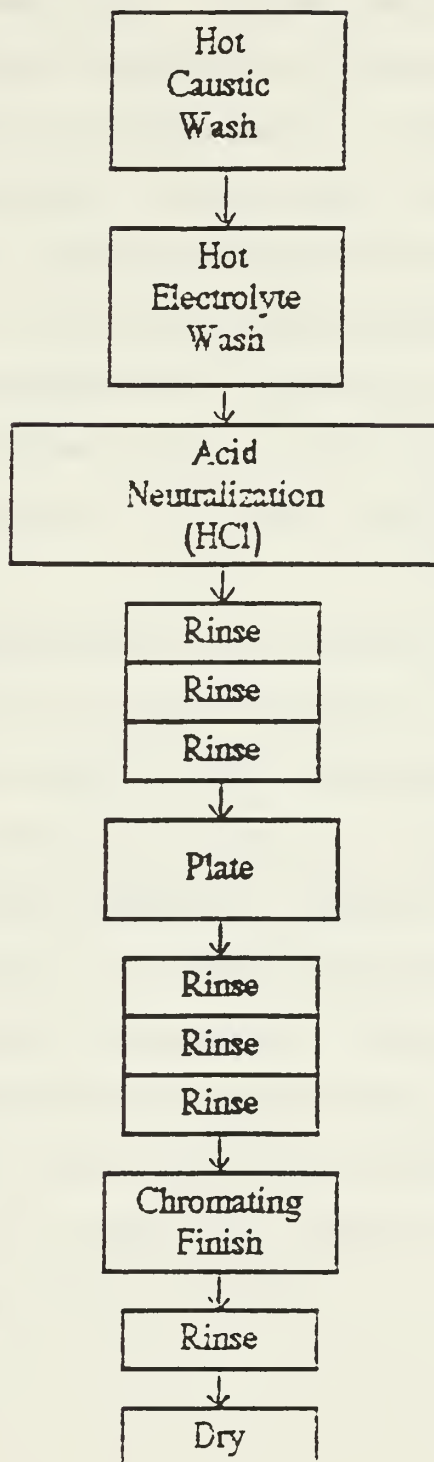
Conventional chromium baths contain 250 to 400 g/L of chromic acid, CrO_3 ; the weight ratio of chromic acid, CrO_3 , to sulfate, SO_4^{-2} , can be varied from 75:1 to 150:1 but is usually kept at approximately 100:1. Bath temperature should be between 32 and 50°C and cathode current density is best at approximately 1450 amps per square meter.(1,11,16) Table 1.4 summarizes the characteristics of bath compositions and operating conditions for chromium plating at four different plating activities.

The standard arrangement for chrome plating process line includes a combination of the following steps: wash, acid neutralization, rinse, plate, finish, dry. A typical process line is depicted in Figure 1.4.

Table 1.4 Chromium Plating Bath Characteristics

Constituent	Bath 1	Bath 2	Bath 3	Bath 4
Chromic Acid CrO_3 , g/L	250	400	340	175
Sulfuric Acid H_2SO_4 , g/L	250	0.0	2.2	1.4
Fluoride Ion F^{-1} , g/L	0.0	0.0	0.0	0.7
Operating Condition				
Temperature, °C	43-49	43-49	54	43-54
Current Density amp/sq cm	0.11-0.23	0.11-0.23	0.16-0.38	0.16-0.46

Figure 1.4
Typical Electroplating Process Line



1.5 Plating Bath Contamination

Chromium plating baths are subject to contamination from various metallic impurities including trivalent chromium, copper, iron, nickel, aluminum, and zinc. Plating facilities also customarily house polishing, grinding, or blasting operations which are frequent sources of contaminants. Other important sources of impurities include: makeup water, rinse water drag-in, cathodic etching, and dissolution of bus bars, racks, and fixtures. Figure 1.5 illustrates the possible sources of chromium plating bath contamination. Dissolution of parts and reuse of water from the chrome plating ventilation systems are the primary sources of iron at U. S. Navy plating activities (17).

Contamination of chromium plating baths by metallic impurities is responsible for various defects in the plating process. Metal impurities pose the most difficult problem to chromium plating and, as such, the removal of representative metals was evaluated in this research. The two most prevalent metallic contaminants found in functional chromium baths, iron and copper (18), were chosen for analysis. The deleterious effects of these foreign metals are summarized in Table 1.5 (17,18). Industry experts have differing opinions concerning the tolerable levels of metallic impurities whether present alone or in combination with other such impurities.

Figure 1.5
Sources of Chromium Plating Bath Contamination

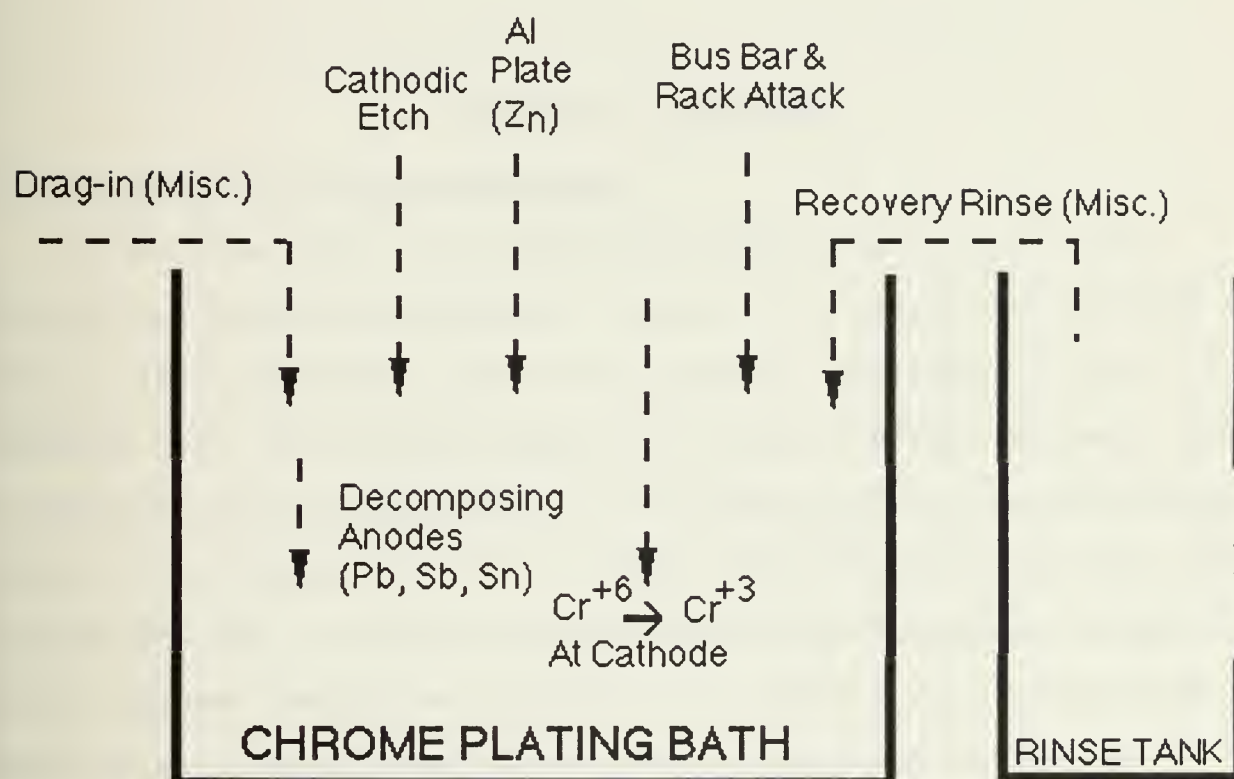


Table 1.5 Effects of Copper and Iron Contamination

- 1) Increased resistance to flow of current
- 2) Decreased bright range
- 3) Increased tendency of burnt deposit
- 4) Rough and pitted deposits
- 5) Reduced covering power
- 6) Reduced adhesion; brittle chromium
- 7) Interference with catalyst balance

2.0 REVIEW OF LITERATURE

2.1 Principles of Electrodialysis

Electrodialysis can be defined as the transport of ions through ion permeable membranes caused by an electrical driving force. Electrodialysis units are normally comprised of two chambers - (1) an anolyte compartment which contains an anode and an aqueous anolyte comprised of the soluble salt of a multivalent cation or a mixture of salts of multi- and monovalent cations and anions and, (2) a catholyte compartment which contains a cathode and an aqueous catholyte comprised of a soluble salt of an acid which forms a water soluble salt of a multivalent cation and agents which insolubilize multivalent cations. These chambers are separated by a selective membrane which is specific or permeable to only one type of ion (cation or anion).

Mass transfer through these selective membranes is a two-step process (19):

(1) reduction of salt concentration in the anolyte by electrotransport of ions from the boundary layer near the membrane, and

(2) diffusion of ions to the partially desalinated boundary layer.

The kinetics of the first step is given by the Nernst equation

$$J_e = (t_m - t_s)i/F, \quad [1]$$

where J_e = Ion flux by electrotransport (g eq/sec cm²)
 t_m = Transport number of ion in membrane
 t_s = Transport number of ion in solution
 i = Current density (mA/cm²)
 F = Faraday number (96,500 C/g eq)

The second step is described by Fick's First law:

$$J_D = D(C_b - C_w)/\delta \quad [2]$$

J_D = Ion flux by diffusion (g eq/sec cm²)
 D = Diffusion coefficient (cm²/sec)
 C_b = Solution concentration
 C_w = Solution concentration at the boundary layer
 δ = Thickness of boundary layer (cm)

The thickness of the boundary layer δ is a function of the linear velocity of the solution in the cell and the geometry of the cell (19). A simple model of the transport phenomena occurring at the membrane surface is shown in Figure 2.1.1

Under steady-state conditions,

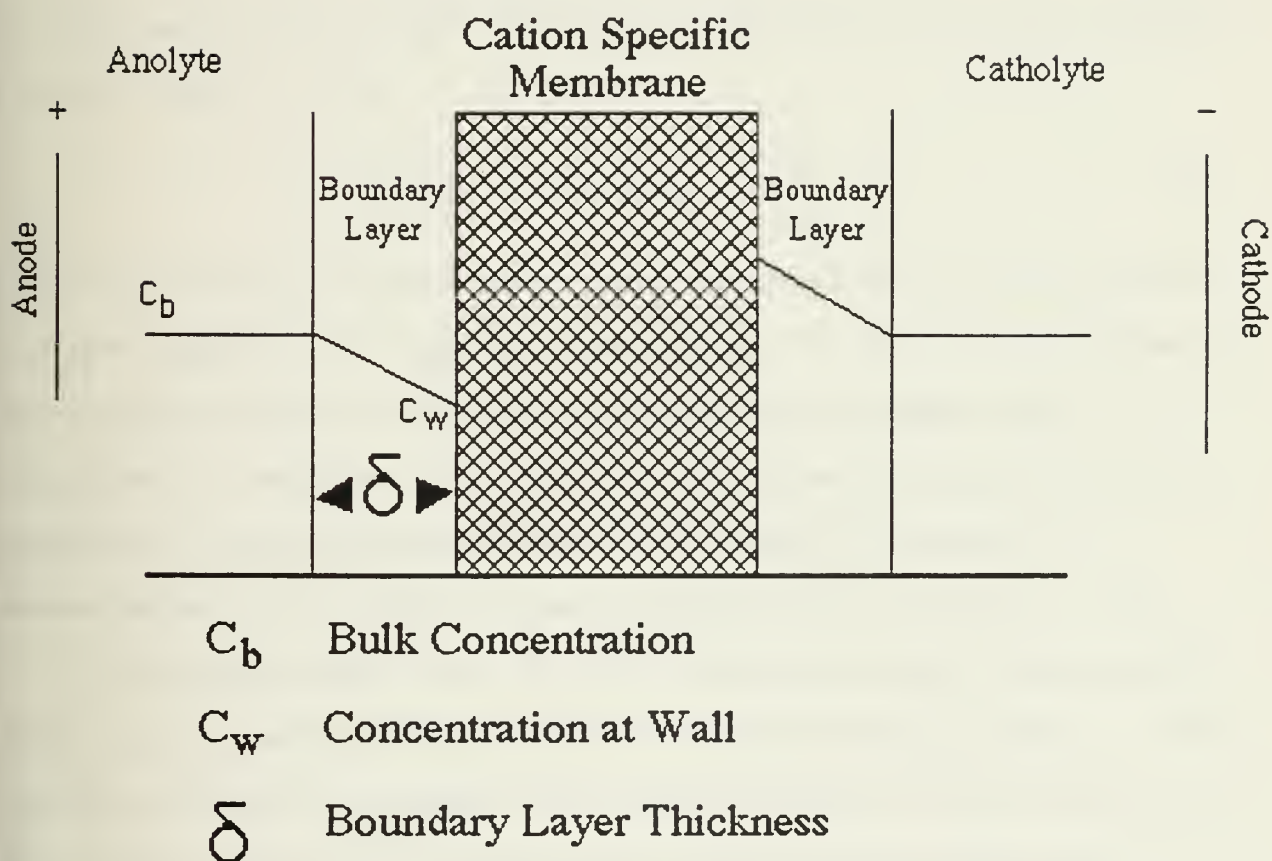
$$J_e = J_D \quad [3]$$

From equations [1] - [3], the following equation can be derived:

$$i = DF(C_b - C_w)/\delta(t_m - t_s). \quad [4]$$

Increasing the voltage supplied to the electrodialytic unit

Figure 2.1.1
Transport Phenomena at the Cation-Specific
Membrane in Electrodialysis



raises the current density. With this increase, ion flux by electrotransport also increases until the concentration of the solution in the boundary layer approaches zero ($C_w = 0$). Ion flux by diffusion is maximized:

$$J_{D(\max)} = DC/\delta, \quad [5]$$

At this point the current density is referred to as the limiting current density (20):

$$i_{(\lim)} = DFC/\delta(t_m - t_s). \quad [6]$$

As the voltage is raised above what corresponds to the limiting current density, the apparent resistance in the cell increases and large amounts of voltage are required to cause small increases in current. In order to safely avoid that situation, commercial electrodialysis units are usually operated at approximately 70 to 80% of the limiting current density (20).

The diffusional flux, J_D , can only be further increased by actually decreasing the thickness of the boundary layer, δ . This can be achieved by raising the linear velocity of the solution in the unit to a level at which the pressure drop across the membrane will not cause leakage.

Mass transfer in an electrodialysis unit is at its highest value when

$$J_e = J_{D(\max)} \quad [7]$$

Further increase in unit voltage will raise current density which

will result mostly in dissociation of water rather than mass transfer of contaminant ions from anolyte to catholyte (19).

The specific membrane surface area required to reduce the metals concentration from C_1 to C_2 can be expressed by the equation

$$A = 0.224(C_1 - C_2)/i\eta_e \quad [8]$$

where i = current density
 C_1 = initial concentration
 C_2 = final concentration
 A = membrane surface area
 η_e = electrical efficiency

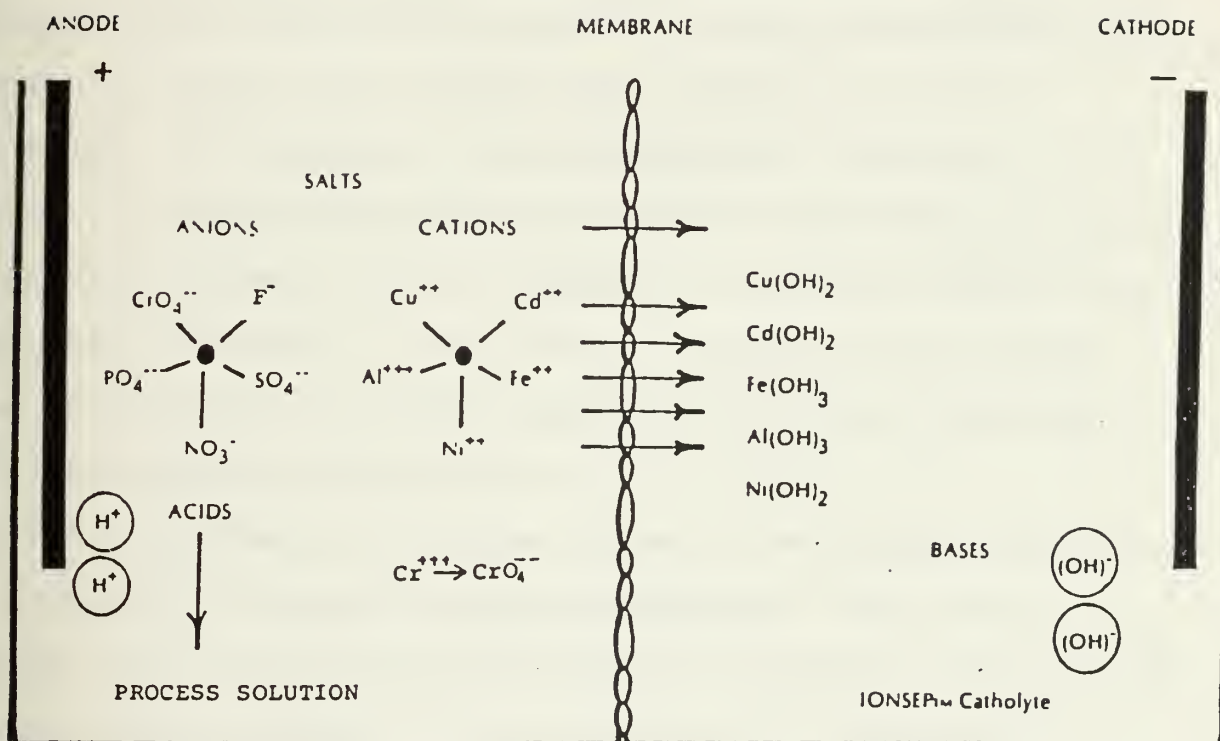
The application of electrodialysis for purification of contaminated chromium plating solutions requires that cation-specific membranes are utilized. These cation-specific membranes have a distribution of fixed, negative charges in a polymer matrix which are permeable to cations. The membranes are comprised of hydrocarbon and halocarbon polymers which contain acids and acid derivatives. They must be able to withstand the chemical conditions of the process and be mechanically suitable for design and economic operation in the electrodialytic process.

When electric current is applied to the cell, the cations are attracted to the negatively charged cathode and flow through the cation-permeable membrane into the catholyte while the membrane and the attractive force of the anode restrict the flow of anions, keeping them in the plating solution. In industrial electrodialysis units a dilute acid solution normally is pumped

through the cathode compartment of the cell and the solution to be purified is pumped through the anode compartment.

The idea of electrodialysis using a caustic catholyte solution is conversion of salts in aqueous solutions into the respective acids of the anions and the hydroxides or insoluble salts of the multivalent cations. This conversion is accomplished through electrodialysis and electrotransport of the cations through the cation-specific membrane into the aqueous catholyte solution which contains agents that both insolubilize or ionically immobilize the cations and soluble salt of an acid (21). The anions of the multivalent cation salt remain in the anolyte and are converted to their acids. Figure 2.1.2 is a simplified illustration of the process. Fouling of the membrane is minimized in the proprietary catholyte through the presence of added salts. This should also contribute to the absence of electrodeposition of metals on the cathode and a higher level of electrodialytic conversion efficiency and capacity (21).

Figure 2.1.2
Electrodialytic Removal of Metal Cations



2.2 Application of Electrodialysis

Electrodialysis has been developed in the past 35 years mostly for the purpose of removing salt from brackish and sea waters with total dissolved solids concentrations ranging from 1000 to 35,000 ppm (19). In the last 20 years electrodialysis and other membrane processes have been applied to wastewater treatment. Some of these industrial applications for electrodialysis have been the removal of salts from cheese whey, treatment of boiler feed waters, acid recovery in steel processing, and phosphoric acid concentration (19,20,22). In contrast, chrome plating bath purification using electrodialysis with caustic catholyte is an innovative application having first been used in the mid to late 1980's to convert remove various metal contaminants (including copper and iron) and counteract trivalent chromium build-up (12).

The proprietary unit tested claims to be broadly useful for the treatment of several different processes. The area of interest for this study was its ability to purify a chromic acid plating solution typical of those used in U. S. Navy plating shops. The specific goal of the research was to determine to what extent the electrodialytic process provided by the manufacturer's technology could remove common metal impurities from a contaminated chromic acid plating bath and how the technology could be practically applied. Additional goals were to determine the characteristic rates of removal in relation to concentration of impurities, recommended time of electrodialysis, and the sizing requirements for industrial application.

3.0 EXPERIMENTAL METHODS AND MATERIALS

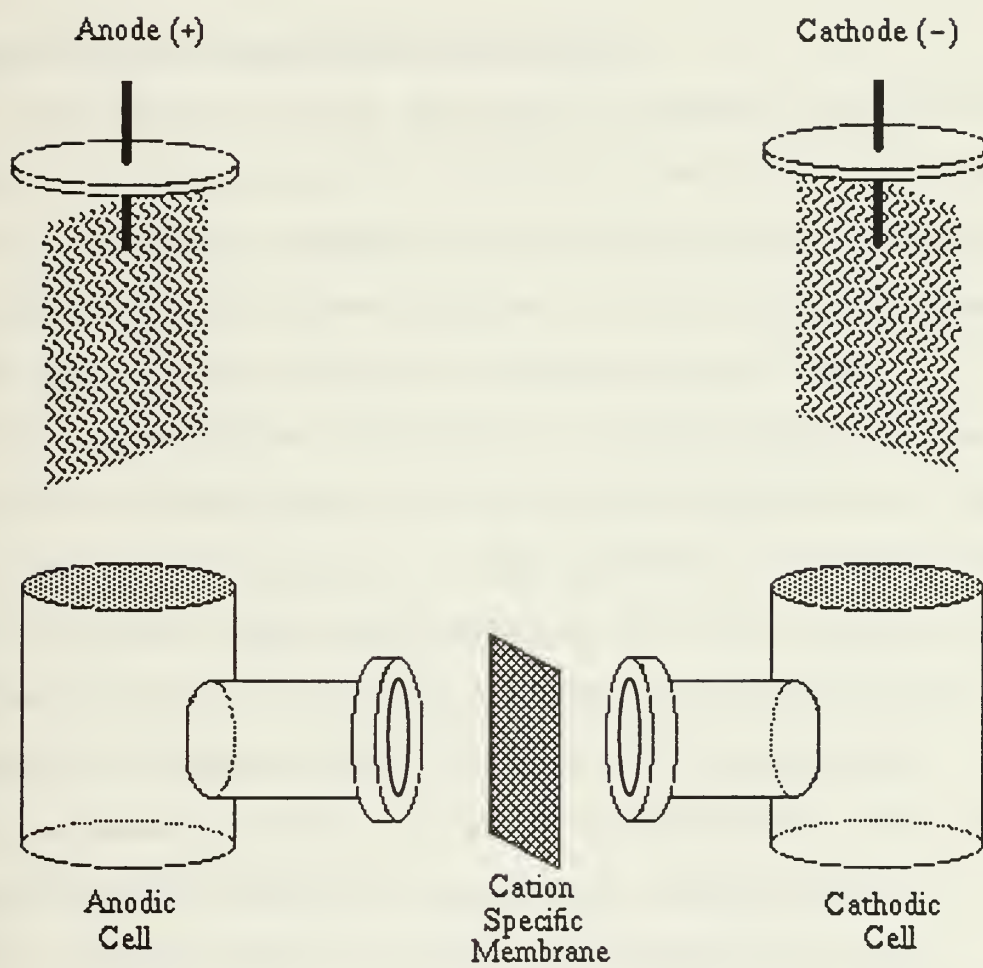
3.1 Experimental Apparatus

Electrodialytic removal of copper and iron contamination from a chromic acid plating bath was performed using a proprietary bench-scale electrodialytic purification unit (IONSEP™ 2C Mini Cell) provided by the manufacturer for experimental purposes. The unit was composed of two chambers, one containing a cathode, the other an anode, separated by a selective membrane (cation specific). Figure 3.1 depicts the experimental unit. Experimental volumes were limited to 25 Ml because of the small size of the respective chambers of the unit provided. The cell's design limited the mode of treatment to a batch scheme.

Following the recommendations of the unit's inventor (23) each test procedure began with a 25 ml sample of the contaminated chromic acid solution being placed in the anode compartment along with 20 ml of the proprietary catholyte solution (a mixture of sodium sulfate and sodium carbonate) being added to the cathode compartment.

Experiments were conducted at room temperature (approximately 25 °C) and solution temperature ranged from 40 to 50 °C due to the evolution of heat at the electrodes. The proprietary anode and cathode were both approximately 9.12 square centimeters in size and constructed in a lattice-like design for increased surface area. The membrane used was a perfluorinated cation specific membrane (Nafion®, manufactured by DuPont). Membrane surface area was 1.77 square centimeters. The total

Figure 3.1
Experimental Unit (IONSEP™ 2C Mini Cell)



anode to cathode gap was 8.4 centimeters. The unit was operated at fixed current, variable voltage with power supplied by a McGean-Rohco, Inc. (Cleveland, Ohio) rectifier at approximately 0.45 amperes which translates into a current density of 490 amperes per square meter based on electrode size. Voltage varied from approximately 8 to 18 volts.

3.2 Preparation of Experimental Solutions

The experimental plating solution or chromic acid solution was prepared by dissolving 350 g of CrO_3 in deionized water and diluting the resultant mixture to one liter with deionized water. This concentration was chosen because it falls within recommended ranges for each of the following characteristics: good conductivity, good current efficiency, satisfactory deposits, and stable solution composition (24) and is representative of those used in industry, including U. S. Navy plating facilities (25). To this solution was added approximately 3.5 g of sulfuric acid which serves as the SO_4^{2-} catalyst and gave the desired 100:1 chromic acid to sulfate weight ratio in the plating bath.

Various amounts of iron or copper contamination were added to the base plating solution to represent plating bath impurities. Higher levels of these contaminants than are normally encountered in operational plating baths were used for experimental purposes. Iron was added in the form of pure iron dust dissolved in small amounts of concentrated hydrochloric acid and copper was added in the form of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

The IONSEP™ caustic catholyte solution was prepared by

dissolving 20 grams of the proprietary mixture of sodium sulfate and sodium carbonate into 100 ml of deionized water.(23)

3.3 Sample Analysis

Atomic absorption (AA) spectrophotometry was used in the quantitative analyses of solutions for metal content in both the preliminary quality assurance/quality control (QA/QC) work and the actual experimental samples. Analyses were performed using a Perkin-Elmer Atomic Absorption Spectrophotometer, Model 303 (Norwalk, Connecticut).

The Cu analyses were conducted using a hollow-cathode Cu lamp (Fisher-Scientific Type 4536024) and an air-acetylene flame. Burner types and orientation were tested to ensure the proper instrument sensitivity for the samples to be analyzed. Calibration of the instrument was accomplished using standard Cu solutions of five different concentrations (2, 4, 6, 8, 10, and 12 mg/L Cu). The Cu solutions were prepared from a standard stock solution (Cu 1000 mg/L, Fisher-Scientific SC194-500) and diluted to proper concentrations. A typical calibration curve for Cu is shown in Figure 3.3.1.

The Fe analyses were conducted using a hollow-cathode Fe lamp (Fisher-Scientific Type 45-36018) and an air-acetylene flame. As with the Cu analysis, burner types and orientation were tested to ensure the proper instrument sensitivity for the Fe containing samples to be analyzed. Calibration of the instrument was accomplished using standard Fe solutions of five different concentrations (2, 4, 6, 8, 10, and 12 mg/L Fe). The

Figure 3.3.1
Typical Cu Standard Calibration Curve

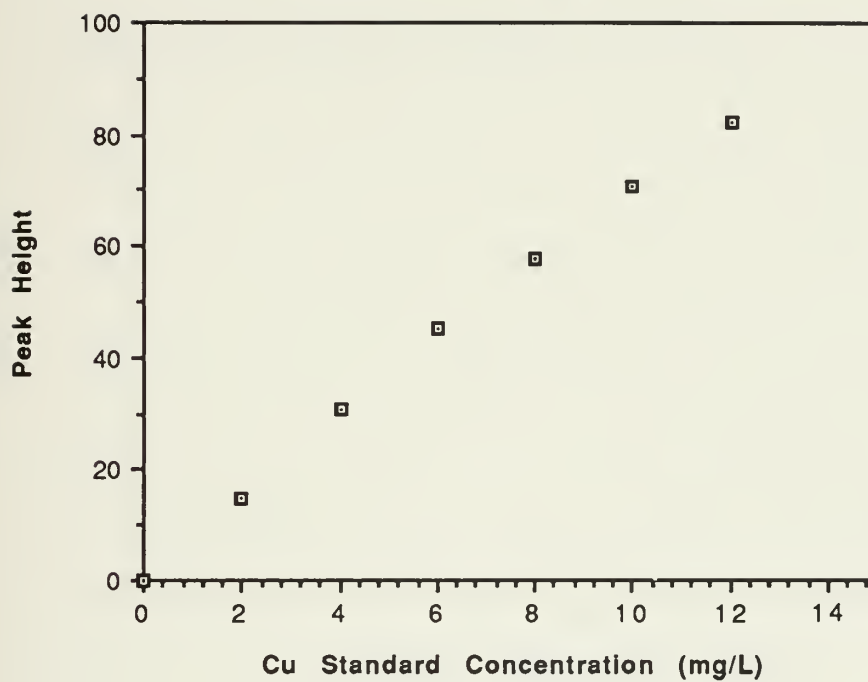
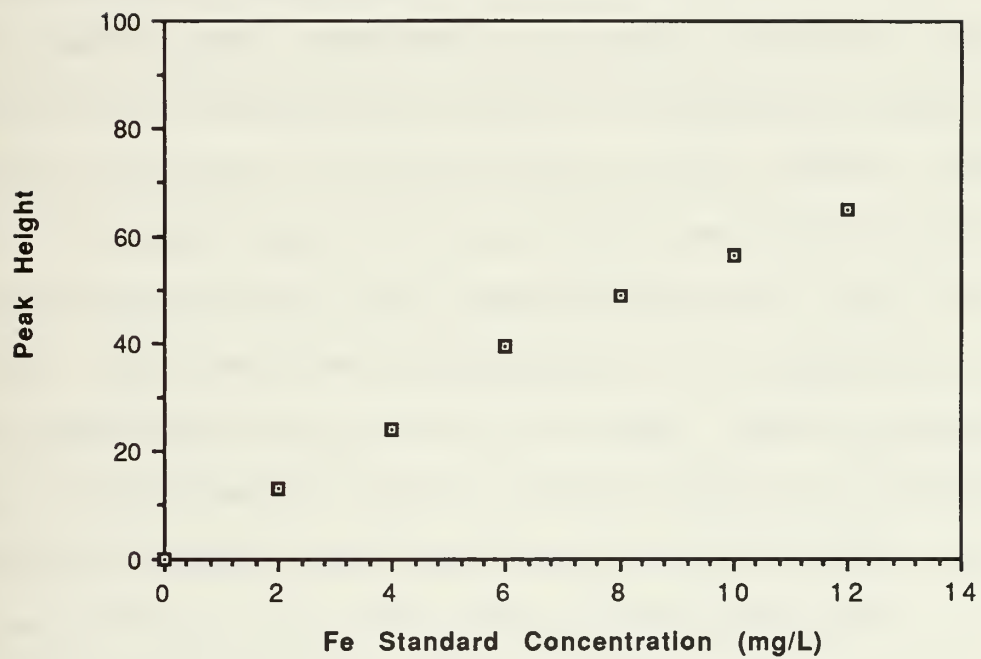


Figure 3.3.2
Typical Fe Standard Calibration Curve



Fe solutions were prepared from a standard stock solution (Fe 1000 mg/L, Fisher-Scientific SI124-500) and diluted to proper concentrations. A typical calibration curve for Fe is shown in Figure 3.3.2.

3.4 Standard Test Conditions

Experiments were conducted with respect to either time or concentration to determine the levels of effective contaminant removal and the kinetic characteristics of the removal. IONSEP™ personnel indicated that the recommended operating time for evaluation of the 2C Mini cell demonstration unit was 18 to 36 hours (26). Only one electrodialysis unit was available which limited experimental runs to one at a time. Due to the small volumes of contaminated plating solutions being run through the experimental apparatus and mass balance accountability, no samples were taken during the course of the individual experiments; only the final solutions were analyzed. At approximately 8 hour intervals the electrodialytic unit was shut off for several minutes to allow for the addition of deionized water to the anolyte side of the apparatus to compensate for the migration of small amounts of water from the anodic chamber to the cathodic chamber. The membrane was not 100% impermeable and the action of electropumping, or the migration of the respective waters of hydration with the cations, permitted this transfer of water through the chambers via the semi-permeable membrane. This practice did not affect the analysis of final metals concentration in either the catholyte or the anolyte as the

initial mass of the contaminant metals was known in both solutions. Subsequent dilution(s) of experimental solutions was performed such that the sum of the final concentrations of the contaminant metal in both solutions would be equal to that of the initial concentration in the plating solution (anolyte).

All samples were analyzed within 24 hours (most within 6 hours) of final dilution. Both the anolyte and catholyte were analyzed for metal concentration using atomic absorption spectrophotometry.

3.5 Experimental Reproducibility

With few exceptions, each experiment was conducted in its entirety three separate times. Atomic Absorption analysis for each experimental sample was performed at least in duplicate.

An initial quality assurance/quality control (QA/QC) program was devised to establish the validity and accuracy of analytical techniques as they were to be applied to experimental sample analysis. QA/QC tests were conducted on the metals Cu and Fe. Contaminant/spiking solutions were prepared for each metal, respectively. Based on the findings of the Hull Cell tests (discussed later), with respect to threshold contaminant levels, the following concentration spreads were spiked into both deionized (DI) water and chromic acid plating solution:

Cu : 1.5, 3.0, and 4.5 g/L

Fe : 3.0, 5.0, and 7.0 g/L

Analyses were performed using the atomic absorption spectrophotometer. Calibration curves for each contaminant were

generated through analysis of the standard stock solutions. A Fisher-Scientific (Fair Lawn, New Jersey) Cu^{2+} Standard Solution of one mg per one mL was used to prepare the various copper standards used in the quality assurance/quality control (QA/QC) phases of the experiments.

A Fisher-Scientific (Fair Lawn, New Jersey) Fe^{3+} Standard Solution of one mg per one mL was used to prepare the various iron standards used in the quality assurance/quality control (QA/QC) phases of the experiments.

Per cent recoveries (in terms of concentration) and standard deviations were based on data obtained from four runs. The larger the standard deviation, the larger the spread of the gathered data. The results of the QA/QC experiments for both copper and iron are shown in Tables 3.5.1 and 3.5.2.

The experimental reproducibility of the copper analyses was very consistent. Per cent standard deviations were below 2% for all concentrations in both deionized (DI) water and chromic acid plating solution. The per cent standard deviations for iron were low as well - below 3% for all concentrations in both solutions. Per cent recoveries for iron in DI water and plating solution were also consistent and extremely reproducible, however, they were surprisingly high (approximately 124% for DI water spikes and approximately 166% for plating solution spikes). Subsequent tests for copper and iron content in uncontaminated plating solution indicated they were not present.

At this point iron was being added to the respective solutions as iron sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$). It was hypothesized that

**Table 3.5.1 Results of QA/QC Experiments for Copper
at Threshold Contaminant Levels**

DI Water:

Level	Recovery (%)	Standard Deviation (ppm)	Per cent Deviation
Low (1500 ppm)	99.6	10.4	0.691
Threshold (3000 ppm)	99.3	32.7	1.09
High (4500 ppm)	99.5	20.4	0.453

Plating Solution:

Level	Recovery (%)	Standard Deviation (ppm)	Per cent Deviation
Low (1500 ppm)	111	21.0	1.40
Threshold (3000 ppm)	111	30.0	1.00
High (4500 ppm)	110	75.5	1.68

**Table 3.5.2 Results of QA/QC Experiments for Iron
at Threshold Contaminant Levels**

DI Water:

Level	Recovery (%)	Standard Deviation (ppm)	Per cent Deviation
Low (3000 ppm)	120	15.8	0.528
Threshold (5000 ppm)	127	17.5	0.350
High (7000 ppm)	126	118	1.69

Plating Solution:

Level	Recovery (%)	Standard Deviation (ppm)	Per cent Deviation
Low (3000 ppm)	166	23.6	0.788
Threshold (5000 ppm)	169	15.2	0.304
High (7000 ppm)	165	192	2.74

the iron sulfate being used may have been dehydrated thus increasing the actual amount of Fe being added to a solution. In order to provide a basis for comparison of iron recovery, pure iron dust was substituted as the source of iron contamination. Standardized solutions ranging from 2 mg/L to 12 mg/L of iron were prepared using both deionized water and the actual plating solution and the results compared to stock iron standard solution dilutions using calibration curves. The subsequent analysis performed using the AA showed that per cent recoveries using the pure iron dust as the source of iron contamination proved to be much lower - 101% for Fe in DI water and 109% for Fe in plating solution. These results are summarized in Table 3.5.3. Based on these findings Fe contamination was added to the test chromic acid solution in the form of the pure Fe dust during the remainder of experimental procedures.

Table 3.5.3 Per Cent Recoveries for Iron Dust Contaminated Samples

Fe Conc.	Standard Solution Run 1/Run 2	Deionized Water (% Recovery)	Plating Solution (% Recovery)
0 mg/L	0.00/0.00	0.00/0.00	0.00/0.00
2 mg/L	9.91/9.69	9.97/9.97 (101%)	10.7/10.5 (108%)
4 mg/L	21.7/21.4	22.2/22.4 (103%)	22.9/23.5 (108%)
6 mg/L	32.9/32.2	33.2/32.5 (101%)	34.9/35.1 (108%)
8 mg/L	44.3/41.6	44.5/42.6 (101%)	48.9/45.5 (110%)
10 mg/L	55.0/52.1	55.0/53.1 (101%)	59.9/57.3 (109%)
12 mg/L	64.1/60.2	64.3/60.5 (100%)	69.9/65.7 (109%)

Average Fe Recovery in DI Water: 101%

Average Fe Recovery in Plating Solution: 109%

3.6 Laboratory Methods

3.6.1 Hull Cell Testing -

The Hull Cell (U. S. Patent 2,149,344) provides a simple and accurate method of conducting plating tests on various plating baths. The Hull Cell apparatus is essentially a miniature electroplating unit that was developed to aid the individual electroplater in characterizing, maintaining, and optimizing quality plating through plating bath control. Because of its ingenious design it enables the operator to determine the condition of the respective plating bath with respect to the limits of the bright current density range, the approximate concentrations of the primary constituents, the concentration of addition agents, the approximate concentrations of organic or metallic impurities, or other plating bath variations. This is usually done through visual analysis of Hull Cell test cathodes after being electroplated in the apparatus.

In this research the Hull Cell apparatus was used to establish Threshold Contamination Levels (TCLs), the level at which the quality of electroplate begins to deteriorate, in the chromic acid bath for Cu and Fe. Trial and error use of the Hull Cell as well as consultation with personnel experienced in the field (25,26,27) were utilized in the approximate determination of these concentrations for Cu and Fe. The TCLs determined during Hull Cell analysis were 3.0 g/L for Cu and 5.0 g/L for Fe. respectively. The descriptive results of the Hull Cell test plates are listed in Tables 3.6.1 and 3.6.2. By knowing the levels

Table 3.6.1 Hull Cell Results for Cu Contamination

Cu Added (g/L)	Bright Plate	Bright w/ Streaking	Dull/ Grey	Blister	No Plate
1	0-72mm	73-85mm	--	86-92mm	93-100mm
1	0-71mm	72-82mm	83-94mm	--	95-100mm
1.5	0-71mm	72-84mm	85-88mm	--	89-100mm
2	0-67mm	68-79mm	--	80-87mm	88-100mm
2.5	0-50mm	51-60mm	61-69mm	69-75mm	76-100mm
3	0-17mm	18-29mm	--	30-43mm	44-100mm

Table 3.6.2 Hull Cell Results for Fe Contamination

Fe Added (g/L)	Bright Plate	Bright w/ Streaking	Dull/ Grey	Blister	No Plate
0	0-70mm	71-86mm	--	--	87-100mm
1	0-62mm	53-73mm	75-84mm	--	95-100mm
1.5	0-55mm	56-74mm	75-84mm	85-94mm	95-100mm
2	0-52mm	53-73mm	74-80mm	81-90mm	91-100mm
2.5	0-49mm	50-70mm	74-80mm	81-98mm	89-100mm
3	0-47mm	48-65mm	66-77mm	78-85mm	89-100mm
3.5	0-46mm	47-61mm	62-69mm	--	70-100mm
4	0-49mm	45-58mm	59-66mm	--	67-100mm
4.5	0-33mm	34-42mm	43-53mm	54-64mm	89-100mm
5	0-10mm	11-14mm	--	15-23mm	24-100mm

of contaminants in the test bath for each plating run and visually comparing the resultant cathodes and their plating characteristics, the concentration of those contaminants where deterioration in the quality of electroplate began to occur was recorded and used in the experimental procedures to follow.

3.6.2 Electrodialytic Removal Using the IONSEP™ 2C Mini Cell -

In the first experiment copper was the contaminant to be electrodialytically removed from the chromic acid plating solution or anolyte. The IONSEP™ 2C Mini Cell electrodialysis unit provided was used for experimental removal. A characterization of the kinetics of contaminant removal was the goal. In the copper experiments the initial concentration of copper was 4500 mg/L which was determined to be a contamination level slightly above the TCL approximated through preliminary Hull cell plating tests. The IONSEP™ catholyte solution was prepared in accordance with the manufacturer's specifications and contained no copper initially. 25 mL of the anolyte (chromic acid solution) was added into the anodic chamber and 20 mL of the IONSEP™ catholyte was added into the cathodic chamber. The anode and cathode were positioned in their respective chambers and connected to a rectifier which provided an amperage of approximately 0.45 amps for the duration of the experimental run. Invariably, through the course of an experimental run a small amount of water was electropumped from the chromic acid to the catholyte resulting in a volume reduction of the anolyte. In

order to maintain a constant volume of anolyte small amounts of DI water were added to the anolyte periodically. At the outset, the anolyte was a deep maroon in color and the catholyte was colorless. When the electrodialytic unit was turned on the evolution of gases immediately occurred at both electrodes and small amounts of red-brown precipitate formed in the catholyte. The catholyte solution itself remained colorless. As the experiment continued more precipitation occurred. The precipitate settled to the bottom of the cathode cell and the catholyte lost some of its clarity. As the experimental run proceeded the anolyte became lighter in color. Some minor precipitation did remain on the cathode itself. The initial Cu experiment was run for 24 hours. At the end of electrodialysis samples were prepared from each solution for metals analysis using the atomic absorption spectrophotometer. Sample preparation was accomplished in the following manner:

- Anolyte:**
- transfer anolyte to clean container
 - rinse anode, cell, and anolyte side of membrane and mix rinse water with anolyte in new container
 - dilute entire volume to 1000 mL
 - take 10 mL of this solution and dilute to 100 mL
- Catholyte:**
- transfer catholyte with precipitates to clean container and acidify with concentrated HCl
 - rinse cathode, cell, and catholyte side of membrane and add collected rinse water to catholyte in new container

- dilute entire volume to 1000 mL
- take 10 mL of this solution and dilute to 100 mL

Both samples were then analyzed for Cu content. This same experimental procedure was performed for the additional time periods of 10, 14, 18, 21, and 36 hours. All other variables were held constant.

The second experiment involved the analysis of the electrodialytic removal of iron contamination from the chromic acid plating bath. Focusing on the performance of the electrodialytic unit and the efficiency of removal, the concentration of Fe contamination was varied while the time of removal was held constant at 12 hours. This was the only difference between the experimental procedures used for Cu and Fe. The Cu procedure utilized a constant initial contaminant concentration with a variance in time of electrodialysis, the Fe procedure included a variance in initial contamination concentration with a constant time of electrodialysis. The threshold contamination level for Fe contamination was determined previously to be approximately 5000 mg/L. The initial volumes of anolyte and catholyte used remained 25 mL and 20 mL, respectively. The initial concentrations used in the individual Fe experiments were 3000, 5000, 7000, and 9000 mg/L.

At the beginning of the experiment the appearance of the anolyte was much the same as it had been for the Cu experiments: deep maroon with no transparency. The catholyte was colorless. As soon as power was provided the evolution of gas occurred at

both electrodes (O_2 at the anode, H_2 at the cathode) and precipitation began to appear in the cathodic chamber. The appearance of the precipitate for the Fe experimental runs was fluffy and light green. The apparent volume of the precipitate generated in the Fe experiments was greater than in the previous Cu runs and the catholyte solution became filled with these precipitates over the course of the experimental runs. As was the case with the Cu experiments, water migrated through the membrane from anodic chamber to cathodic chamber due to electropumping and was therefore added to the anolyte in small amounts throughout the course of each experiment. Sample preparation following each experimental run was performed identically to the procedure described for the Cu experiments.

4.0 RESULTS AND DISCUSSION

4.1 The Effect Of Foreign Metal Contamination

The emphasis of this research was on the removal of impurities from the chromium plating bath. Information extracted from the literature indicated that copper (Cu) and iron (Fe) were two of the more prevalent metal contaminants found in electroplating processes and, as such, were chosen to be used in this work. Discussions with individuals at several U. S. Naval electroplating facilities showed this to be particularly true at military plating activities (9,17,25). The deleterious effects on electroplating quality caused by excessive levels of these metals in the test chromium plating bath were seen in the

laboratory through the use of the Hull Cell tests.

The Hull Cell tests provided concrete evidence of the specific effects of foreign substances in an electroplating bath. Using the Hull Cell apparatus as a miniature plating bath allowed one to see the plating problems associated with a contaminated bath. Contaminant levels were introduced into the plating bath in a stepwise fashion and a new test cathode was plated at each subsequent level of contamination. As the critical concentration was approached and surpassed the appearance of each cathode showed the deterioration of the quality and extent of plating taking place. This was evident through visual inspection of the plates as dullness, "rainbowing", streaking, pitting, and areas of no plating were observed on the test cathodes.

In industrial applications contamination of the bath means the electroplating process is placed under stress. Consultation with practicing electroplaters and the literature indicated that opinions vary as to what are considered permissible levels of contamination in any one bath. The requirements placed on a plating activity with regards to quality and quantity of work, whether placed internally or externally, are a major factor in the determination of acceptable plating bath characteristics. The specifications of specialized parts being plated or company policy on quality control are examples of these requirements. Cracking, dullness, and pitting of the chrome finish can occur due to the hardness or brittleness of the resultant chrome plate in an overly contaminated bath and are prime products of stressed electroplating operation through plating bath contamination.

Regardless of the differences in the admissible levels of contamination, there can be no disputing the fact that metallic impurities in plating baths reduce actual plating efficiency, the quality of plating, and increase the cost of the plating process with respect to hazardous waste disposal, inefficient utilization of raw materials and energy, and rework.

4.2 Electrodialytic Removal of Copper Contamination

The copper removal experiments were performed with the only test variable being that of the duration of electrodialysis - all other factors (sample volumes tested, amperage applied, and concentration of Cu contamination) were held constant. Other variables such as anode, cathode, and membrane surface area were constant throughout all experimental procedures as they were fixed characteristics of the available electrodialytic unit. The goal was to characterize the kinetics of removal and to determine if there existed a period or periods of time when electrodialytic removal was at an optimum. The characteristics of removal would be studied with respect to removal as a function of time. By gaining insight into these areas one could determine the usefulness of the electrodialytic process for use in the industrial purification of chromium plating process baths. An understanding of the variables involved in proper power and sizing requirements as well as process design should be met.

In general, one of the advertised advantages of electrodialysis and, specifically, the proprietary unit used in this research is the reduction of wastes generated. The increase in

efficiency should result in more reliable processing, more efficient use of chemicals and raw materials, and a nearly closed-loop process. In theory, virtually all metal impurities would be removed and kept at low levels which, in turn, provides more reliable plating at higher plating rates with lower power requirements. The fouling of plating baths through metal contamination is counteracted and kept at a minimum through the electrodialytic removal of the contaminant ions thereby increasing the life of a bath and reducing the costs associated not only with new bath preparation but, more importantly, with the direct costs of proper treatment and disposal of the hazardous wastes generated contaminated plating baths and process waters.

In all of the Cu removal experiments the initial concentration of the contaminant was 4500 mg/L Cu which represented a contaminant level slightly above the TCL (3000 mg/L) approximated from the Hull Cell testing. The time of electrodialysis for the first round of experiments was chosen as 24 hours based on recommendations from IONSEP™ personnel and for ease of accomplishment. For ensuring overall mass balance accountability both the anolyte and catholyte solutions were diluted and analyzed for the presence of Cu. In reporting the extent of removal, the percentage of removal was taken solely from the amount of Cu remaining in the anolyte (plating solution) as that was the area of concern. Prior to electrodialysis the weight of Cu in the anolyte was 112.5 mg and the mass of Cu in the catholyte was 0.0 mg. The subsequent dilution scheme for AA

sample preparation provided for initial concentration of Cu in the anolyte sample prior to electrodialysis to be 11.25 mg/L with the catholyte sample containing no Cu. The dilution scheme for all samples was such that following electrodialysis the total weight of Cu between the two solutions should remain 112.5 mg and the respective concentrations of Cu in the solutions should add up to 11.25 mg/L. Appendix A contains example calculations of the weight of Cu and concentration. Actual per cent recoveries of Cu determined by analyzing both anolyte and catholyte for metal content and mass balance purposes ranged from 92 to 99 %. The small losses experienced were attributable to sample preparation and the fact that the IONSEP™ 2C Mini Cell unit did experience a small amount of electrodeposition on the proprietary cathode. This could have been attributed to a deficiency in the amount of generated hydroxide ions, OH^- , by the cathode to react with the entering cations causing some cations to be drawn to the negative charge of the cathode itself.

The production of a precipitate in the cathode chamber suggested that Cu removal was performed. Atomic Absorption analysis of both the anolyte and catholyte verified that Cu was, indeed, removed during the initial 24 hour experimental periods. The next step was to determine the extent of removal for variable periods of time to gain a better understanding of the capabilities of the electrodialytic unit for Cu removal in the chromium plating bath. With this in mind the following time periods were evaluated as well: 10 hours, 14 hours, 18 hours, 21 hours, and 36 hours. In each of the indicated time frames all

experimental variables, except time of electrodialysis, were kept constant. Table 4.2 shows the experimental data gathered from the electrodialysis of Cu. Appendix A contains the data and sample calculations which were used to generate Table 4.2.

Analysis of these data suggest that this electroalytic removal follows first order kinetics, which is shown graphically in Figure 4.2.1 on a semi log scale. The first order reaction constant under the conditions of this experiment was approximated as 0.0459 hr^{-1} from the first-order equation, $C = C_0 e^{-kt}$. Figure 4.2.2 displays the characteristics of Cu removal with time on a square graphic scale. From this figure the decrease in the rate of removal can be seen as time progressed and Cu concentration diminished. Figure 4.2.3 compares the average rates of removal for each time period of electrodialysis respectively.

Table 4.2 Electrodialytic Removal of Cu

Time (hrs)	Initial Conc. (mg/L)	Final Conc. (mg/L)	Rate of Removal (mg/L-hr)	Removal (%)
36	4500	1010	97.1	77.6
24	4500	1960	131	69.8
24	4500	1570	140	65.2
18	4500	1960	141	56.4
14	4500	2410	149	46.4
10	4500	2910	159	35.3

Figure 4.2.1
Electrodialytic Removal of Cu

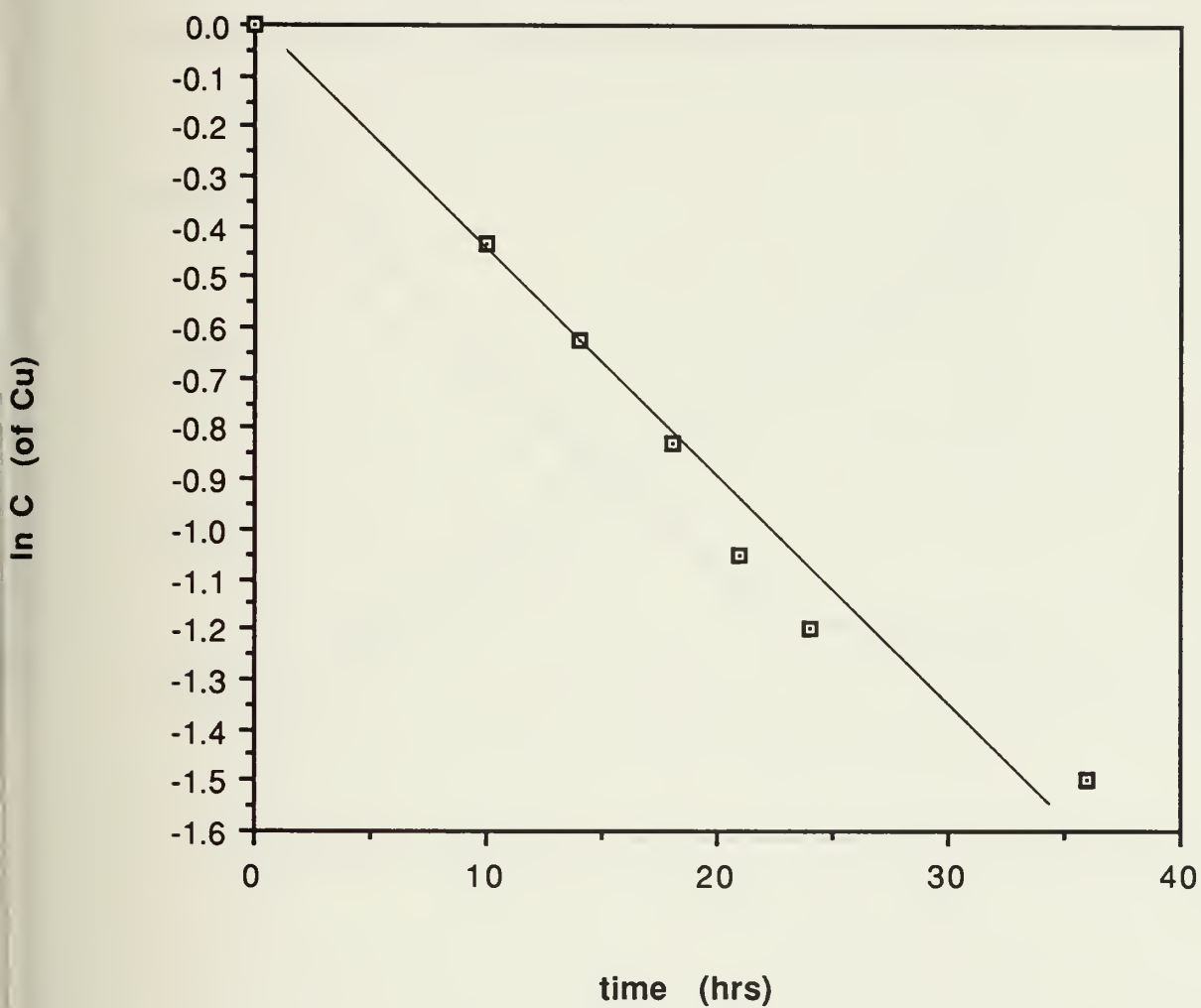


Figure 4.2.2
Cu Removal with Time

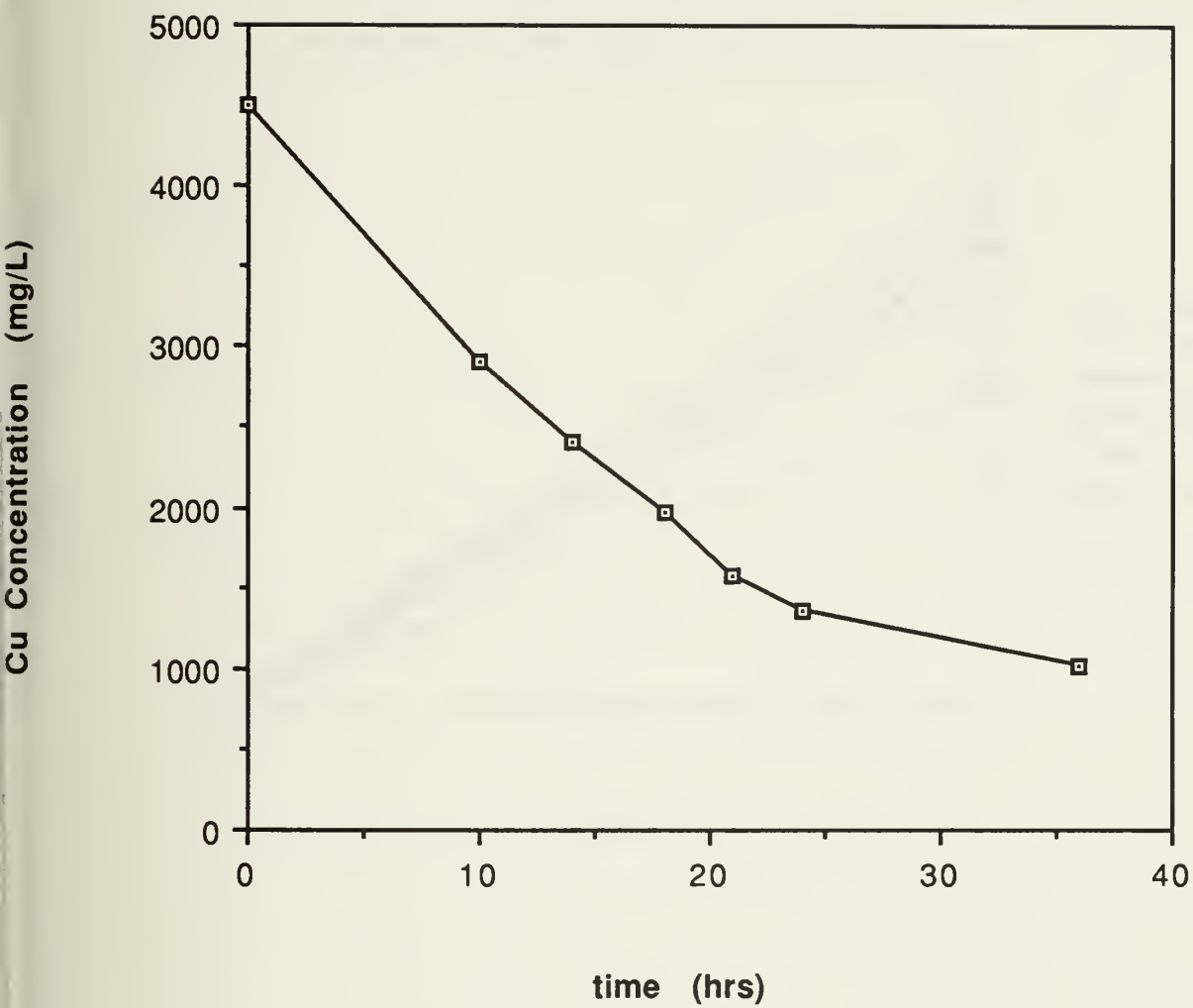
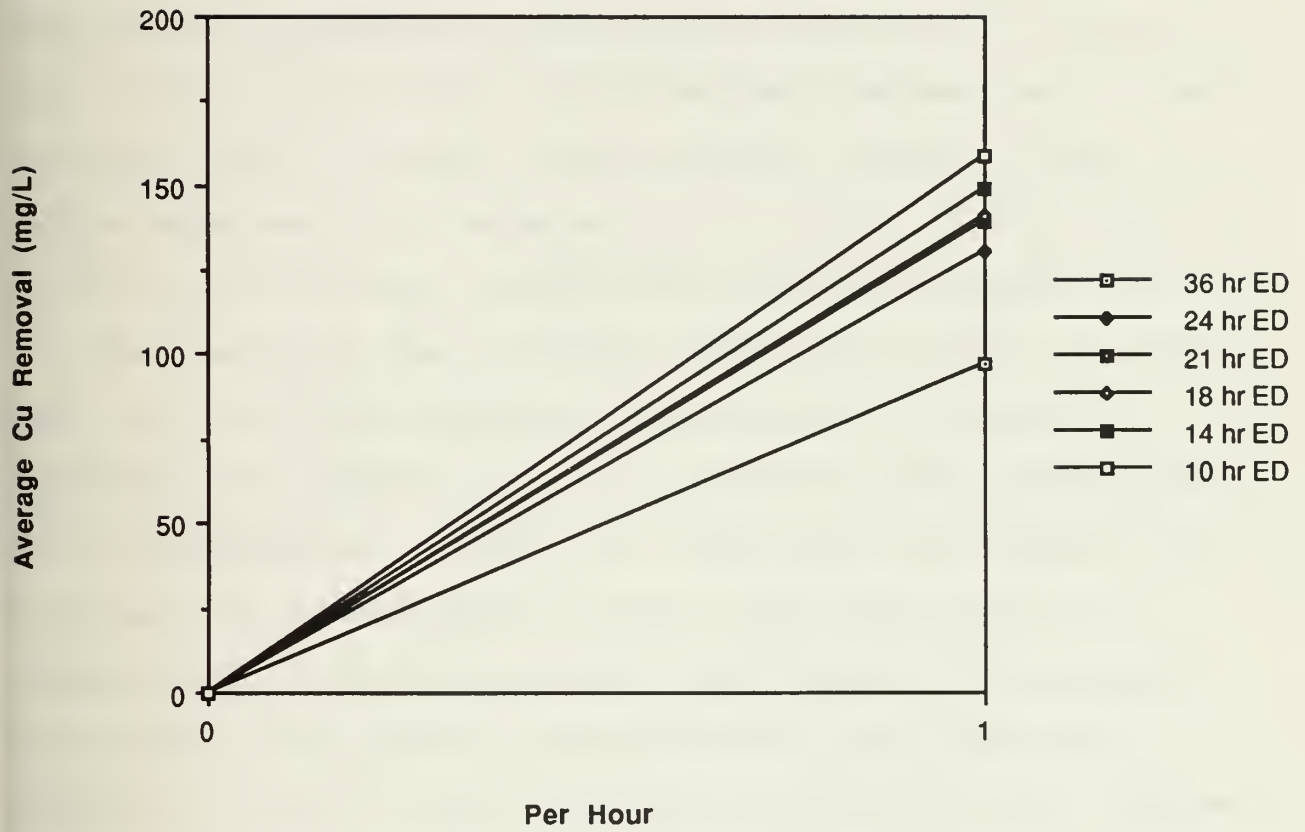


Figure 4.2.3
Average Cu Removal Rate



4.3 Electrodialytic Removal of Iron

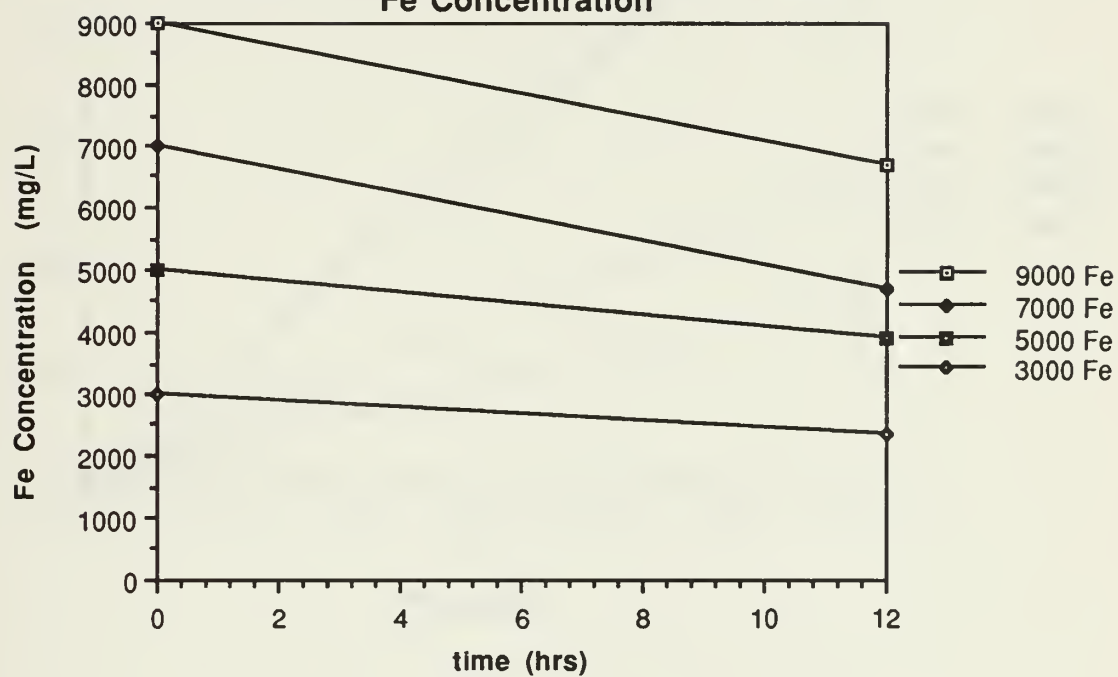
In a variation from the Cu experimental runs it was decided to vary the initial metals concentration for the Fe removal experiments to better characterize the efficiency of removal. The following contaminant concentrations were used: 9.0 g/L, 7.0 g/L, 5.0 g/L, and 3.0 g/L. Variables held constant were: time of electrodialysis - 12 hours, anolyte sample volume - 25 mL, applied amperage - 0.45 amperes, and the inherent sizing features of the unit (anode size, cathode size, membrane surface area).

The results of the Fe removal experiments (Table 4.3) show that, with all other variables held constant, the rate of electrodialytic removal of Fe is a function of the concentration of Fe contamination. Figure 4.3.1 shows that the removal of Fe in terms of Fe concentration per unit time decreases as the concentration of Fe in the chromic acid solution is decreased. The removal of Fe also was characterized by the first-order equation, $C = C_0 e^{-kt}$, which revealed an approximate rate constant of 0.0247 hr^{-1} for the experimental conditions. Perhaps a better representation of removal is shown in Figure 4.3.2 as the removal is characterized by a comparison of the total mass of Fe removed versus time. Figure 4.3.3 is a semi log plot of the initial concentration versus the rate of removal. The slope of this plot is approximately 1.1, again indicating first order removal. Appendix A contains the original data used to generate these tables and figures.

Table 4.3 Electrodialytic Removal of Fe

Time (hrs)	Initial Conc. (mg/L)	Final Conc. (mg/L)	Rate of Removal (mg/L-hr)	Removal (%)
12	9000	6690	193	25.7
12	7000	4710	191	32.7
12	5000	3920	90.2	21.6
12	3000	2340	54.9	22.0

Figure 4.3.1
Average Electrodialytic Removal of Fe:
Fe Concentration



**Figure 4.3.2 Electrodialytic Removal of Fe:
Total Mass of Fe Removed**

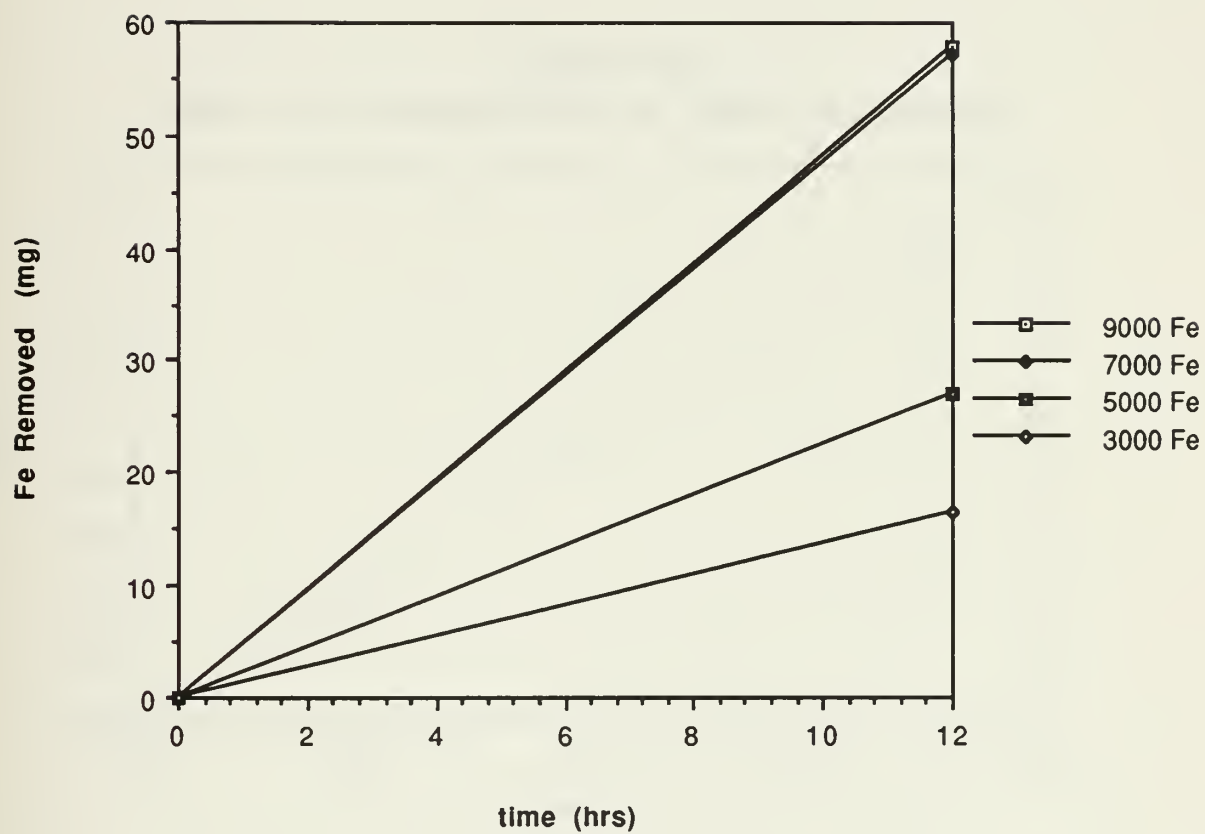
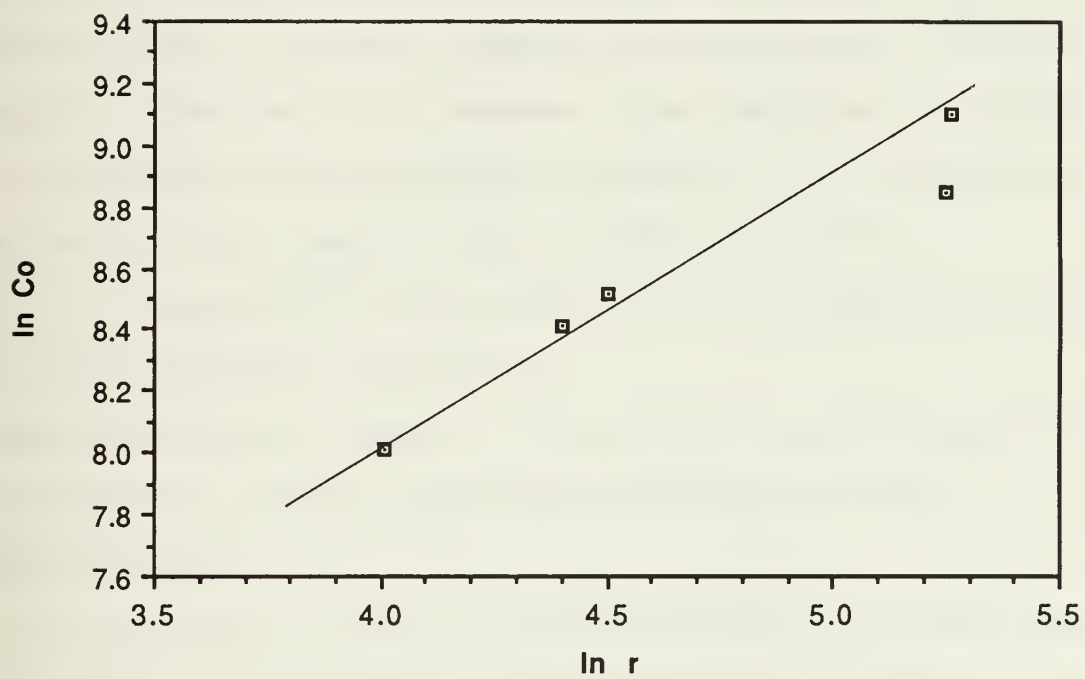


Figure 4.3.3
Initial Fe Concentration vs. Rate of Removal



4.4 Efficiency of Removal

As indicated by the data in Tables 4.2 and 4.3 there is a disparity in the rates of removal for Cu and Fe. Although the experimental variables for each separate run of Cu and Fe removal were never identical it was possible to approximate the values of electrodialytic removal for both metals by interpolation using log values at the following experimental conditions: time of electrodialysis - 12 hours, concentration of metals - 4500 mg/L, and applied amperage - 0.45 amperes. The resultant calculated data is included and highlighted in Table 4.4.1, a compilation of calculated and experimental data for both Cu and Fe. Figure 4.4.1 exhibits the comparison of ionic removal for the metals under identical conditions.

The difference in removal of Cu and Fe can be explained by Faraday's Laws. The two important principles of these fundamentals are:

(1) The weight of metal electrotransported is proportional to the quantity of electricity passed (current x time).

(2) For a given quantity of current, the weight of metal electrotransported is proportional to its chemical equivalent.

The second principle can be shown in the following equation (assuming 100% current efficiency) (11):

$$w = ItA/ZF \quad [9]$$

where

- w = weight of metal (g)
- I = current (A)
- t = time (sec)
- A = atomic weight of metal
- z = valency
- F = Faraday number (96,500 A-sec/g eq)

Table 4.4.1 Compiled Data for Metals Removal

Cu:

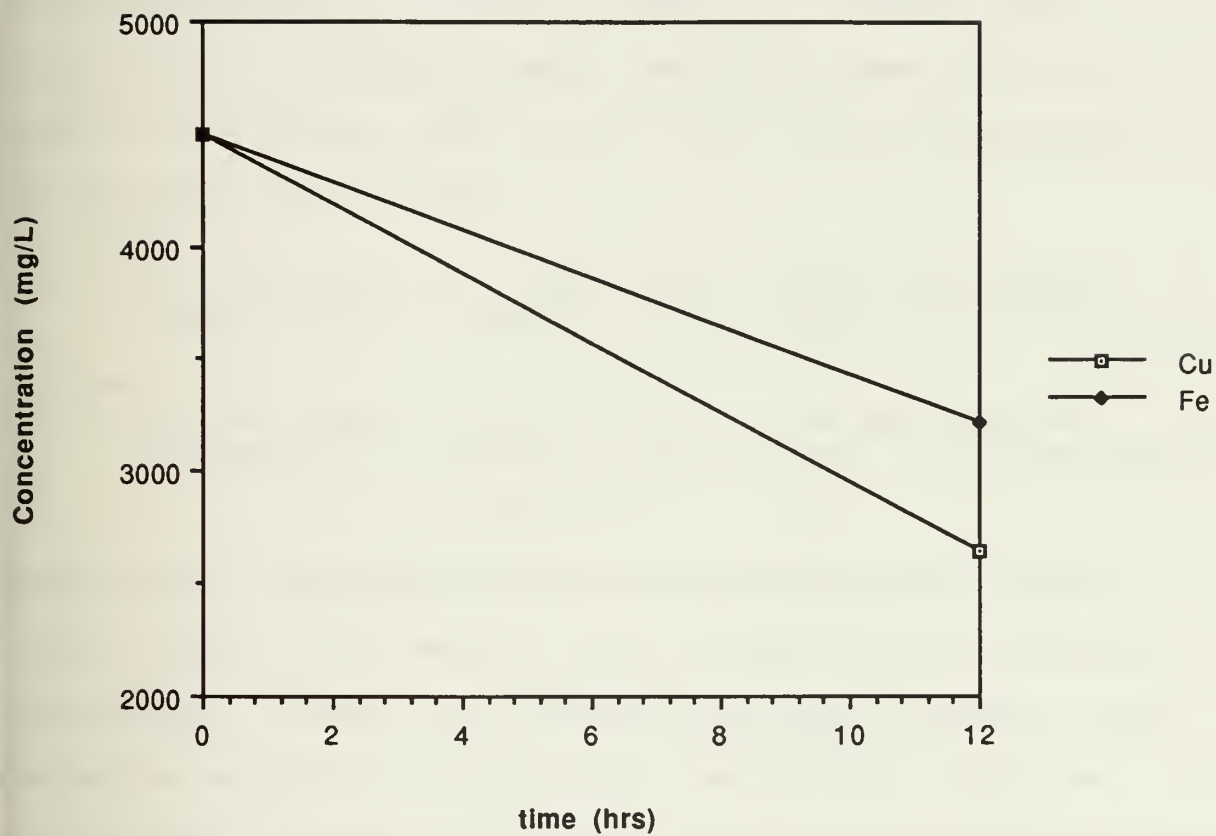
Time (hrs)	Initial Conc. (mg/L)	Final Conc. (mg/L)	Rate of Removal (mg/L-hr)	Removal (%)
36	4500	1010	97.1	77.6
24	4500	1360	131	69.8
21	4500	1570	140	65.2
18	4500	1360	140	56.4
14	4500	2410	149	46.4
12	4500*	2650*	154*	41.1*
10	4500	2910	159	35.3

Fe:

Time (hrs)	Initial Conc. (mg/L)	Final Conc. (mg/L)	Rate of Removal (mg/L-hr)	Removal (%)
12	9000	6690	193	25.7
12	7000	4710	131	32.7
12	9000	3920	90.2	21.6
12	4500*	3520*	81.5*	21.7*
12	3000	2340	54.9	22.0

Note: Calculated values are indicated by *

Figure 4.4.1
Comparison of Electrodialytic Removal
(metals concentration vs. time)



Using equation [9] to solve for the average efficiency for each experimental run gave the results listed in Table 4.4.2.

The chemical equivalent of Cu^{2+} is 31.77 and the chemical equivalent of Fe^{3+} is 18.61, a mass ratio of 1.71 (Cu) to 1 (Fe).

The calculated data included in Table 4.4.1 verify this relationship to Faraday's Laws. The actual mass ratio of Cu removal to Fe removal was 1.89 (Cu) to 1 (Fe) as determined by the following calculations:

Cu -

$$\begin{aligned} C_o (4500 \text{ mg/L}) - C (2650 \text{ mg/L}) &= 1850 \text{ mg/L removed} \\ 1850 \text{ mg/L} \times 1 \text{ L/1000 mL} \times 25 \text{ mL sample} &= 46.25 \text{ mg removed} \end{aligned}$$

Fe -

$$\begin{aligned} C_o (4500 \text{ mg/L}) - C (3520 \text{ mg/L}) &= 980 \text{ mg/L removed} \\ 980 \text{ mg/L} \times 1 \text{ L/1000 mL} \times 25 \text{ mL sample} &= 24.50 \text{ mg removed} \end{aligned}$$

$$46.25/24.50 = 1.89$$

These values represent the mass electrotransported from an initial mass of 112.5 mg per anolyte sample of both Cu and Fe, respectively. Figure 4.4.2 shows this change in mass of the respective metals over the 12 hour test period. The same relationship is shown when change in metals concentration over the 12 hour time period is compared (Figure 4.4.1).

The average efficiency of removal at the different experimental conditions studied is listed for each metal, respectively, in Table 4.4.2. Higher levels of efficiency for Fe removal are found at higher ionic concentrations. Higher average efficiencies are also indicated for the shorter Cu removal periods. Both of these instances show that as the ionic concentration approaches zero the efficiency of removal will

Table 4.4.2 Average Efficiency for Cu and Fe Removal**Cu:**

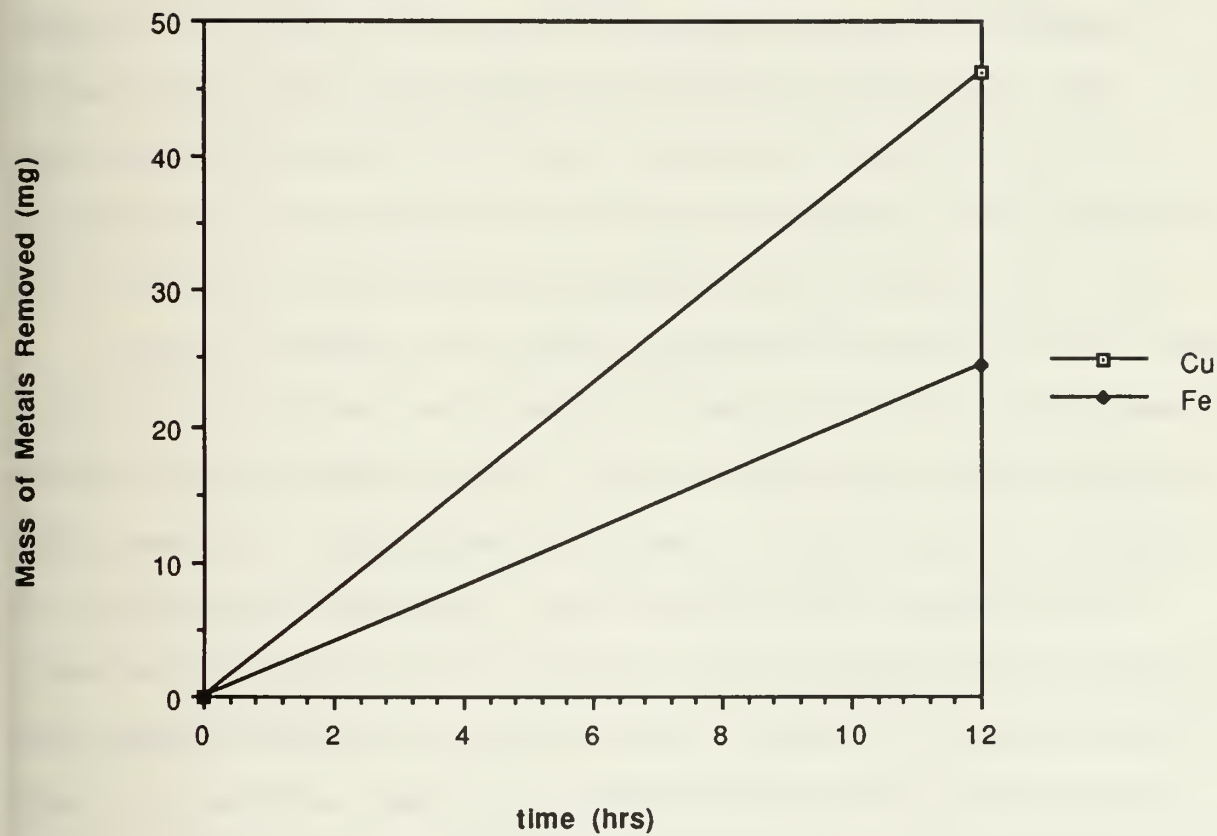
Time (hrs)	Average Efficiency (%)
36	.51
21	.68
21	.72
18	.74
14	.78
12*	.81*
10	.83

Fe:

Concentration (mg/L)	Average Efficiency (%)
9000	1.73
7000	1.71
9000	.81
4500*	.73*
3000	.49

Note: Calculated values are indicated by *

Figure 4.4.2
Comparison of Electrodialytic Removal
(Mass of Metals Removed vs. Time)



approach zero as more hydronium ions are electrotransported in direct competition with the contaminant metals. The electro-dialytic process itself continues to operate at the same rate of ion transport no matter what the concentration of metal cations is. That is to say, in general, there is a balance between the cations and anions generated in the unit. The electrical efficiency for metal contaminant metal removal is essentially a comparison of the electrotransport of H^+ (and other cations) versus the electrotransport of Cu^{2+} and/or Fe^{3+} (26).

The efficiency of the bench scale electro-dialysis unit used in this research was decreased by several factors. The anode-to-cathode gap was much greater than in industrial units causing a requirement for significantly higher voltages needed to supply the recommended amperage. Also, although the cationic flow generated by the electric potential and the Brownian movement of the solution generally provide proper levels of mixing without requiring external means, the shape of the cell used (Figure 3.1.1), with the relatively long "neck" pathways to the membrane, counteracted some of that mixing. Build-up of excessive volumes of the precipitated metal hydroxides in the cationic chamber also could serve as a limiting factor as the electrical processes involved in the transport and reaction of the ions was inhibited by crowding. The appearance of some electrodeposition on the cathode as well as some fouling of the membrane adversely affected removal. Finally, the unit is operated at current densities significantly lower than those found in industrial applications which adds to the dominant tendency of H^+ transport.

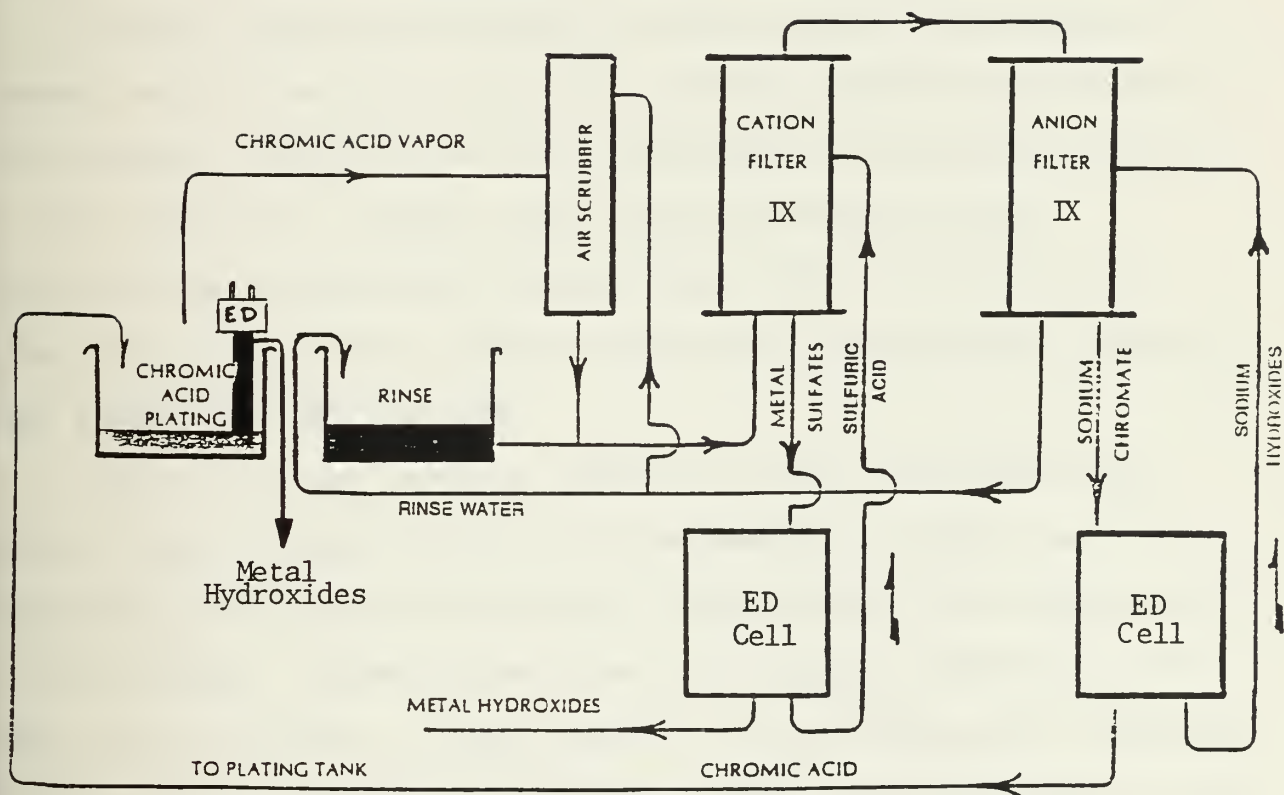
5.0 CONCLUSIONS AND RECOMMENDATIONS

The application of electrodialysis using caustic catholyte appears to be a viable and cost effective method of chromium plating bath purification at high levels of metal contamination. For plating facilities requiring chromic acid baths with contaminant metals content well below the TCLs approximated in this research (3 g/L Cu and 5 g/L Fe) it would not be recommended. The removal of metal cations below these levels is low due to the first order reaction kinetics.

When using electrodialysis in industrial plating baths it is recommended for continuous, uninterrupted operation. This research used a bench scale unit for batch-type treatment in finite periods. Because of this difference in operational application better removal efficiencies could be expected in industrial settings. Additionally, electrical inefficiencies, cell design problems, and build-up of excessive hydroxides should be lessened in optimally designed electrodialysis units. These process improvements typically would result in an increase in efficiency of approximately 5 to 10% of efficiency experienced with the experimental unit.

Figure 5.0 represents a possible closed-loop system using electrodialysis. In this research, the removal of metal cations using electrodialysis was studied. Successful application of electrodialysis to a closed-loop system such as that depicted in Figure 5.0 would also be contingent on its ability to convert trivalent chromium to chromic acid and to purify the acid and base solutions used to regenerate the in-line ion-exchange

Figure 5.0
Example Closed-Loop System



resins. Additional research into these areas is needed to assess the feasibility of such a closed-loop process of chromium plating bath treatment and resource recovery. Purification in concert with evaporative technology for concentration of already concentrated, low volumes of chromic acid bath could be effective.

It was originally intended to study the characteristics of removal using electrodialysis in a chromic acid bath contaminated with multiple metals as well as the singular situations presented in this research. Further study of the process and the electrochemistry involved indicated that there would not be a synergistically adverse effect on removal efficiencies, therefore that aspect was not pursued.

The role of the caustic catholyte in the electrodialytic process was to reduce fouling of the membrane, enable the precipitation of metal hydroxides, and minimize electrodeposition on the cathode. Observations from this research indicate that these goals were met to some extent, but not completely realized. Minor amounts of membrane fouling and wear was experienced as was electrodeposition on the cathode. The impacts on process efficiency were not measured in this research.

The basis of the this research was to determine the ability of electrodialysis with caustic catholyte to purify chromic acid plating solutions thus prolonging bath life and minimizing hazardous waste. As tested in this research, the effective application of electrodialysis for these purposes is limited to

highly contaminated chromic acid baths that can tolerate total metals concentrations of above 3 g/L or in the use of an on-line unit to maintain bath contaminant levels just below the TCLs.

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APPENDIX A

Sample Calculations and Data

I. Sample Characteristics

Initial Mass of Cu:

$$4500 \text{ mg Cu/L} \times 25 \text{ mL} \times 1 \text{ L/1000 mL} = 112.5 \text{ mg Cu}$$

Dilution Scheme:

$$\text{Dilution I: } 112.5 \text{ mg Cu/L} \times 1/1 \text{ L} = 112.5 \text{ mg Cu/L}$$

$$\text{Dilution II: } 112.5 \text{ mg Cu/L} \times 10 \text{ mL} \times 1/100 \text{ mL} = 11.25 \text{ mg/L}$$

II. Electrodialytic Removal of Cu

- 36 Hours

Cu IONSEP 36 Hr Run #1
10 AUG 90

Anolyte Conc.: 2.61 mg/L
Cath. Conc.: 8.53 mg/L
Total Cu Conc: 11.14 mg/L
Initial Cu: 11.25 mg/L
Cu Recovery: 99.0 %
Cu Removal: 76.8 %

Cu IONSEP 36 Hr Run #2
13 AUG 90

Anolyte Conc.: 2.42 mg/L
Cath. Conc.: 7.65 mg/L
Total Cu Conc: 10.07 mg/L
Initial Cu: 11.25 mg/L
Cu Recovery: 89.5 %
Cu Removal: 78.5 %

Average Cu Recovery: 94.2 %
Average Cu Removal: 77.6 %

- 24 Hours

Cu IONSEP 24 Hr Run #1
31 JUL 90

Anolyte Conc.: 3.40 mg/L
Cath. Conc.: 7.13 mg/L
Total Cu Conc: 10.53 mg/L
Initial Cu: 11.25 mg/L
Cu Recovery: 93.6 %
Cu Removal: 69.8 %

Cu IONSEP 24 Hr Run #2
02 AUG 90

Anolyte Conc.: 3.57 mg/L
Cath. Conc.: 7.05 mg/L
Total Cu Conc: 10.62 mg/L
Initial Cu: 11.25 mg/L
Cu Recovery: 94.4 %
Cu Removal: 68.3 %

Cu IONSEP Run #3
6 AUG 90

Anolyte Conc.: 3.24 mg/L
Cath. Conc.: 7.16 mg/L
Total Cu Conc: 10.40 mg/L
Initial Cu: 11.25 mg/L
Cu Recovery: 92.4 %
Cu Removal: 71.2 %

Average Cu Recovery: 93.5 %
Average Cu Removal: 69.8 %

- 18 Hours

Cu IONSEP 18 Hr Run #1
28 Aug 90

Anolyte Conc.: 4.81 mg/L
Cath. Conc.: 5.38 mg/L
Total Cu Conc: 10.19 mg/L
Initial Cu: 11.25 mg/L
Cu Recovery: 90.6 %
Cu Removal: 57.1 %

Cu IONSEP 18 Hr Run #2
29 AUG 90

Anolyte Conc.: 4.91 mg/L
Cath. Conc.: 5.34 mg/L
Total Cu Conc: 10.25 mg/L
Initial Cu: 11.25 mg/L
Cu Recovery: 91.1 %
Cu Removal: 56.5 %

Cu IONSEP 18 Hr Run #3
30 AUG 90

Anolyte Conc.: 4.98 mg/L
Cath. Conc.: 5.28 mg/L
Total Cu Conc: 10.26 mg/L
Initial Cu: 11.25 mg/L
Cu Recovery: 91.2 %
Cu Removal: 55.7 %

Average Cu Recovery: 91.0 %
Average Cu Removal: 56.4 %

- 14 Hours

Cu IONSEP 14 Hr Run #1
22 Aug 90

Anolyte Conc.: 6.16 mg/L
Cath. Conc.: 3.03 mg/L
Total Cu Conc: 9.19 mg/L
Initial Cu: 11.25 mg/L
Cu Recovery: 81.7 %
Cu Removal: 45.2 %

Cu IONSEP 14 Hr Run #2
23 AUG 90

Anolyte Conc.: 5.95 mg/L
Cath. Conc.: 4.27 mg/L
Total Cu Conc: 10.22 mg/L
Initial Cu: 11.25 mg/L
Cu Recovery: 90.8 %
Cu Removal: 47.1 %

Cu IONSEP 14 Hr Run #3
24 AUG 90

Anolyte Conc.: 5.98 mg/L
Cath. Conc.: 3.95 mg/L
Total Cu Conc: 9.93 mg/L
Initial Cu: 11.25 mg/L
Cu Recovery: 88.3 %
Cu Removal: 46.9 %

Average Cu Recovery: 86.9 %
Average Cu Removal: 46.4 %

- 10 Hours

Cu IONSEP 10 Hr Run #1
23 Aug 90

Anolyte Conc.: 7.46 mg/L
Cath. Conc.: 2.16 mg/L
Total Cu Conc: 9.62 mg/L
Initial Cu: 11.25 mg/L
Cu Recovery: 85.5 %
Cu Removal: 33.7 %

Cu IONSEP 10 Hr Run #2
28 AUG 90

Anolyte Conc.: 7.10 mg/L
Cath. Conc.: 3.29 mg/L
Total Cu Conc: 10.39 mg/L
Initial Cu: 11.25 mg/L
Cu Recovery: 92.4 %
Cu Removal: 36.9 %

Average Cu Recovery: 89.0 %
Average Cu Removal: 35.3 %

III. Electrodialytic Removal of Fe

9000 mg/L Fe

Fe 12 Hr-9000 mg/L #1 13 SEP 90	Fe 12 Hr-9000 mg/L #2 23 SEP 90
Anolyte Conc.: 8.43 mg/L	Anolyte Conc.: 8.54 mg/L
Cath. Conc.: 3.18 mg/L	Cath. Conc.: 2.75 mg/L
Total Fe Conc: 11.61 mg/L	Total Fe Conc: 11.29 mg/L
Original Fe: 11.25 mg/L	Original Fe: 11.25 mg/L
Fe Recovery: 103.2 %	Fe Recovery: 100.4 %
Fe Removal: 25.1 %	Fe Removal: 24.1 %

Fe 12 Hr-9000 mg/L #3 24 SEP 90
Anolyte Conc.: 7.46 mg/L
Cath. Conc.: 3.11 mg/L
Total Fe Conc: 10.57 mg/L
Original Fe: 10.35 mg/L
Fe Recovery: 102.1 %
Fe Removal: 27.9 %

Average Cu Recovery: 101.9 %
Average Cu Removal: 25.7 %

Example Calculation:

$9000 \text{ mg/L} \times 25.7\% = 2313 \text{ mg/L removed}$

$2313 \text{ mg/L} \times 1 \text{ L/1000 mL} \times 25 \text{ mL sample} = 57.8 \text{ mg removed}$

7000 mg/L Fe

Fe 12 Hr-7000 mg/L #1
7 SEP 90

Anolyte Conc.: 7.36 mg/L
Cath. Conc.: 2.50 mg/L
Total Fe Conc: 9.86 mg/L
Original Fe: 10.50 mg/L
Fe Recovery: 93.9 %
Fe Removal: 29.9 %

Fe 12 Hr-7000 mg/L #2
11 SEP 90

Anolyte Conc.: 7.17 mg/L
Cath. Conc.: 2.62 mg/L
Total Cu Conc: 9.79 mg/L
Original Fe: 10.50 mg/L
Fe Recovery: 93.2 %
Fe Removal: 31.7 %

Fe 12 Hr-7000 mg/L #3
21 SEP 90

Anolyte Conc.: 6.87 mg/L
Cath. Conc.: 4.19 mg/L
Total Fe Conc: 11.06 mg/L
Original Fe: 10.50 mg/L
Fe Recovery: 105.3 %
Fe Removal: 34.6 %

Fe 12 Hr-7000 mg/L #4
22 SEP 90

Anolyte Conc.: 6.86 mg/L
Cath. Conc.: 4.30 mg/L
Total Fe Conc: 11.16 mg/L
Original Fe: 10.50 mg/L
Fe Recovery: 106.3 %
Fe Removal: 34.7 %

Average Cu Recovery: 99.6 %
Average Cu Removal: 32.7 %

Example Calculation:

$7000 \text{ mg/L} \times 32.7\% = 2289 \text{ mg/L removed}$

$2289 \text{ mg/L} \times 1 \text{ L/1000 mL} \times 25 \text{ mL sample} = 57.2 \text{ mg removed}$

5000 mg/L Fe

Fe 12 Hr-5000 mg/L #1
16 SEP 90

Anolyte Conc.: 7.85 mg/L
Cath. Conc.: 1.77 mg/L
Total Fe Conc: 9.62 mg/L
Original Fe: 10.00 mg/L
Fe Recovery: 96.2 %
Fe Removal: 21.5 %

Fe 12 Hr-5000 mg/L #2
17 SEP 90

Anolyte Conc.: 7.80 mg/L
Cath. Conc.: 1.90 mg/L
Total Fe Conc: 9.70 mg/L
Original Fe: 10.00 mg/L
Fe Recovery: 97.0 %
Fe Removal: 22.0 %

Fe 12 Hr-5000 mg/L #3
25 SEP 90

Anolyte Conc.: 7.80 mg/L
Cath. Conc.: 1.78 mg/L
Total Fe Conc: 9.58 mg/L
Original Fe: 10.00 mg/L
Fe Recovery: 95.8 %
Fe Removal: 22.0 %

Fe 12 Hr-5000 mg/L #4
26 SEP 90

Anolyte Conc.: 7.26 mg/L
Cath. Conc.: 1.86 mg/L
Total Fe Conc: 9.12 mg/L
Original Fe: 9.20 mg/L
Fe Recovery: 99.1 %
Fe Removal: 21.1 %

Average Cu Recovery: 97.0 %
Average Cu Removal: 21.6 %

Example Calculation:

$5000 \text{ mg/L} \times 21.6\% = 1080 \text{ mg/L removed}$

$1080 \text{ mg/L} \times 1 \text{ L/1000 mL} \times 25 \text{ mL sample} = 27.0 \text{ mg removed}$

3000 mg/L Fe

Fe 12 Hr-3000 mg/L #1
18 SEP 90

Anolyte Conc.: 8.78 mg/L
Cath. Conc.: 1.68 mg/L
Total Fe Conc: 10.46 mg/L
Original Fe: 11.25 mg/L
Fe Recovery: 93.0 %
Fe Removal: 22.0 %

Fe 12 Hr-5000 mg/L #3
25 SEP 90

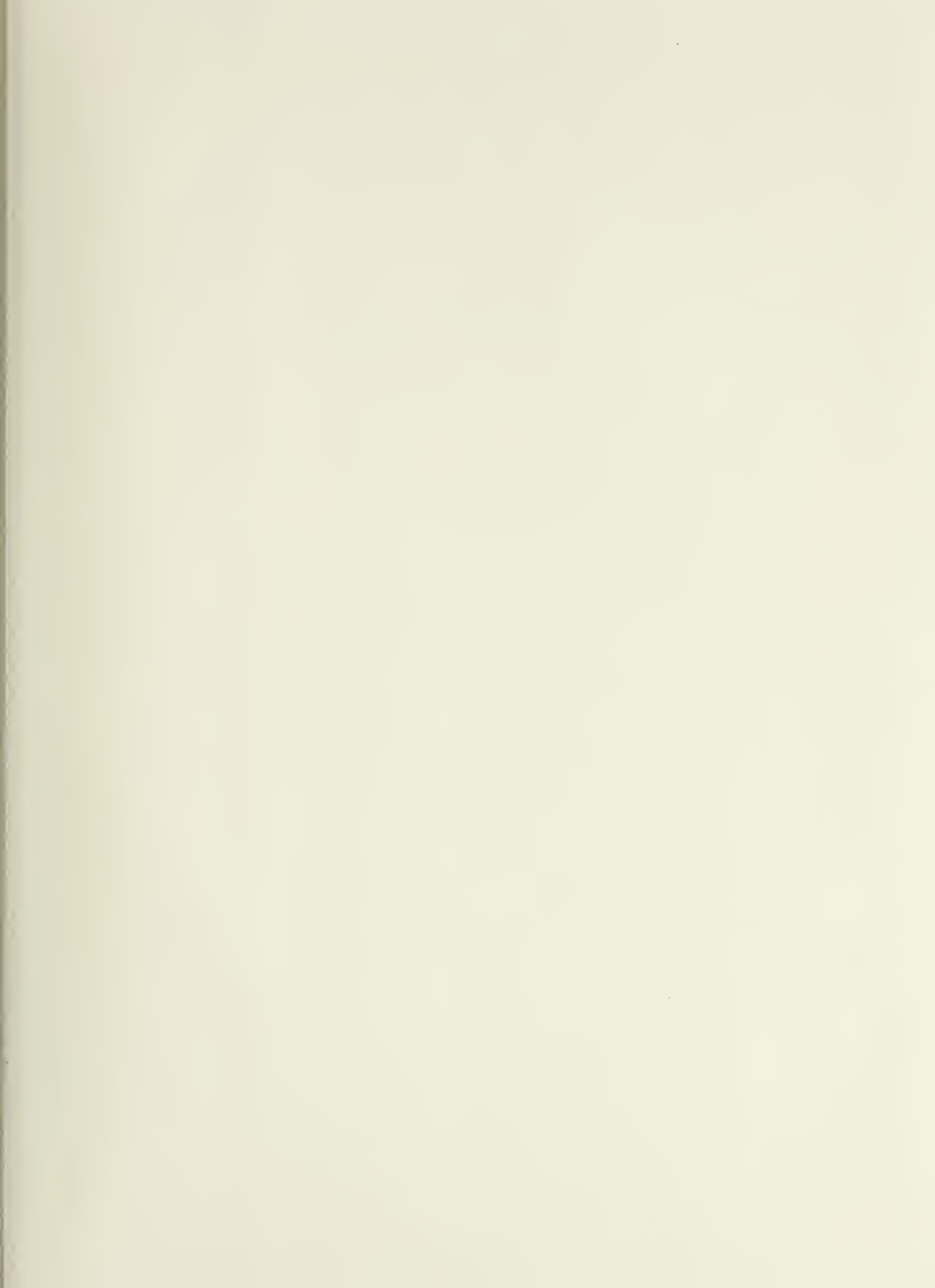
Anolyte Conc.: 8.80 mg/L
Cath. Conc.: 1.46 mg/L
Total Fe Conc: 10.46 mg/L
Original Fe: 11.25 mg/L
Fe Recovery: 91.2 %
Fe Removal: 21.8 %

Average Cu Recovery: 92.1 %
Average Cu Removal: 22.0 %

Example Calculation:

$3000 \text{ mg/L} \times 22.0\% = 660 \text{ mg/L removed}$

$660 \text{ mg/L} \times 1 \text{ L}/1000 \text{ mL} \times 25 \text{ mL sample} = 16.5 \text{ mg removed}$



Thesis
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c.1

Removal of copper and
iron contamination from
chromic acid electro-
plating baths using
electrodialysis with
caustic catholyte.

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